PHOTOCHEMISTRY

OF

AMMONIA AND HYDRAZINE.

BY

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CONTENTS.

Introduction.

One of the fundamental principles of scientific reasoning which have advanced knowledge of the Universe so rapidly is the selection, by inductive processes of thought, of general hypotheses from masses of concomitant observational data. Such general hypotheses, or laws, are considered to be rational correlations of the data if logical deductions from them are experimentally demonstrable. It was the lack of a general hypothesis which retarded the progress of the study of photochemistry until the beginning of this century.

As early as 1768 Scheele had established the fact that the darkening of silver nitrate is promoted in different degrees by different parts of the solar spectrum. But this and other facts remained isolated and uncorrelated observations until Einstein's Law of Photochemical Equivalence in 1911 did for photochemistry what Planck's Quantum Theory had done, a few years earlier,

for the closely allied study of spectroscopy.

The now classical methods of photochemistry of determining the nature of absorption spectra, quantum efficiencies and the influence of wavelength and light intensity have gone a long way towards elucidating the mechanisms of photochemical reactions, by providing a detailed knowledge of the kind and number of molecules, atoms or radicals which are produced in the primary processes and initiate the secondary thermal reactions. Since the direct effect of light ceases in practically every photochemical reaction with the dissociation of the absorbing molecules, the study of photochemistry might be considered as limited to the primary processes. But, in fact, it is more convenient to include the secondary reactions in describing photochemical reactions. Thus the complete study of a photochemical reaction includes the determination of the reaction products, the effects of concentrations of reactants and products as well as other molecules and the part played by the walls of the reaction vessels.

The relation of absorption spectra to photoreactions is the border line between the studies of spectroscopy and photochemistry. But the determination

of the absorption spectra is an essential part of any investigation of photochemical reactions. From an examination of the absorption spectrum of reacting molecules it is possible to determine whether the primary photochemical process is a direct dissociation or an activation of the reacting molecules. When the absorption spectra are discontinuous and show only vibrational and diffuse rotational bands, as in predissociation spectra, the absorbing molecules are generally held to dissociate spontaneously within a very short interval, i.e. 10^{-12} sec., of absorbing the quanta. Recently, however, there has arisen a considerable amount of dubeity as to the correct interpretation of predissociation spectra, particularly with regard to polyatomic molecules such as aldehydes and ketones. Thus it is perhaps best, at the moment, to treat the interpretation of predissociation as rapid dissociation with reserve until it can be confirmed by complete kinetic analysis of the photochemical reaction in question. If the absorption spectra are continuous, there seems to be no doubt that this is evidence of an electronic change accompanied by a vibrational change of sufficient energy to cause dissociation. Where the

electronic change is accompanied by no disturbance of the vibrational and rotational bands third bodies will be required to bring about dissociation. Thus, though it is possible from examination of absorption spectra to state whether dissociation will occur when molecules are radiated with a given wavelength and what are the conditions for dissociation, it is not generally possible to select any one of a number of possible dissociation mechanisms for polyatomic molecules, unless energetic and other conditions are also known.

In any physical investigation of natural phenomena the fundamental objectives to be pursued are cause and effect followed by their quantitative relationship. In photochemistry the third objective was attained by the Law of Photochemical Equivalence. With this law it has been possible to determine the most important characteristic of photochemical reactions, namely, the quantum efficiency. Since photochemical investigations cover the overall reaction it is necessary to distinguish two quantum efficiencies, the primary and the overall efficiencies. In practice the overall efficiency is generally the only one readily determinable and it is usual to assume the quantum efficiency of the primary

process is unity until there is definite evidence against it. Evidence has been accumulating that such an assumption is not so generally valid as has been thought, particularly where polyatomic molecules such as aldehydes and ketones are involved. When a molecule absorbs a quantum it may lose energy by fluorescence, by third body collisions or by internal degradation before dissociation and, in that way, the maximum primary quantum efficiency may not always be attainable. For the overall quantum efficiency to be exactly unity it is necessary for the products of the primary dissociation to be stable molecules but examples are rather rare, one being the dissociation of formaldehyde into hydrogen and carbon monoxide by light of 3000 °A. It is more usual for the primary process to involve the production of atoms or radicals which initiate secondary thermal reactions and consequently overall efficiencies vary from small fractions to large integers. In general the overall photochemical reaction can be rendered schematically by part or the whole of the following:-

$A + h\nu \rightarrow$	1. $A' \rightarrow A + h\nu$	Fluorescence	Primary Process
	2. $A' + M \rightarrow A + M$	Third-body deactivation	
	3. $A' \rightarrow A$	Internal degradation	
	4. $A' \rightarrow B_1 + B_2$	Direct dissociation	
	5. $A' + M \rightarrow B_1 + B_2 + M$	Collision induced dissociation.	

followed by

	6. $B_1 + B_2 + M \rightarrow A + M$	Recombination ($\gamma < 1$)	Thermal Reactions
	7. $B_1 + D \rightarrow A + C$	Reaction regenerating A ($\gamma < 1$)	
	8. $B_1 + B_2 \rightarrow D + C$ $B_1 + B_1 \rightarrow D$ $B_2 + B_2 \rightarrow C$ $B_1 + D \rightarrow C$ etc.	Non-chain reactions ($\gamma = 1$)	
	9. $B_1 + A \rightarrow D + C$	Non-chain reaction with A ($\gamma = 2$ or 3)	
	10. $B_1 + D \rightarrow E + B_2$ $B_2 + C \rightarrow E + B_1$	Chain reactions without A ($\gamma > 1$ or $\gg 1$)	
and/or	11. $B_1 + A \rightarrow D + B_2$ $B_2 + A \rightarrow C + B_1$	Chain reactions with A ($\gamma > 1$ or $\gg 1$)	

With a knowledge of absorption spectra and the quantum efficiencies of photochemical reactions it is thus possible to attempt an interpretation of the mechanisms. Continuous absorption spectra and small integral quantum efficiencies indicate primary processes of Type 4 followed by secondary processes of Type 8 or 9 Large integral quantum efficiencies are an indication of chain reactions, while fractional quantum efficiencies indicate deactivation, recombination, regeneration and/or internal degradation. In order to analyse the reaction mechanisms further it is necessary, in classical photochemical technique, to study the effect of the quantum efficiency of varying pressure of both reactants and foreign inert molecules, light intensity, wavelength, temperature and surface area of the reaction vessels. And, in general, the information about the mechanisms, obtained by these methods, is not unequivocal since it is usually possible to postulate more than one mechanism which would account for the variation produced in the quantum efficiency.

The limitations of the classical methods of photochemistry have led to the development of special techniques which, in some instances, have a fairly wide

application but in others are almost specifically applicable to the question in mind. Examples[42] of the former class of special technique are the employment of heavy hydrogen as an indicator in reactions involving the movement of hydrogen atoms and the use of the para-ortho hydrogen conversion as a means of measuring the concentration of atomic hydrogen produced in such reactions. To the latter class belong the techniques such as the inhibition of direct photochemical decomposition of ammonia[6] and phosphine[43-44] by mercury sensitised production of atomic hydrogen from molecular hydrogen, this technique being specifically designed to investigate the role played by atomic hydrogen in the direct decompositions. It is the purpose of this thesis to describe the results of special techniques of both classes to the elucidation of the kinetics of photochemical reactions, with special reference to ammonia and hydrazine.

The photodecomposition of ammonia was one of the first reactions to which the Law of Photochemical Equivalence was applied but the reaction kinetics of it are by no means completely elucidated yet. In 1912 Warburg[4] determined the quantum efficiency as 0.25, a

value which has been substantially confirmed by more recent determinations of 0.1 to 0.3 according to conditions. The absorption spectrum of ammonia consists of completely diffuse bands in the region 2250-1800 ° A and Bonhoeffer and Farkas[3] interpret these bands as evidence of predissociation. The absence of fluorescence, even at low pressures, which has been reported by Rabinowitch and Wood,[4] seems to confirm that this diffuseness is due to the formation of a short lived excited state which decomposes spontaneously. The quantum efficiency of this primary process has been taken as unity. The dissociation may take place by one of two mechanisms,

$$NH_3 + h\nu \rightarrow (NH_3)' \rightarrow NH_2 + H \quad \ldots\ldots\ldots (1)$$

$$NH_3 + h\nu \rightarrow (NH_3)'' \rightarrow NH + H_2 \quad \ldots\ldots\ldots (2)$$

Energetic considerations provide no distinction but electronic selection rules rather favour (2) since the sum of the normal states of NH and H_2 corresponds to that of excited NH_3. However, studies of the overall reaction, particularly the absence of influence of molecular hydrogen at ordinary temperatures, indicate that (1) is more likely and it is generally accepted as

the primary process. The most definite evidence for the production of atomic hydrogen as an intermediate in the decomposition has been found by Geib and Harteck[5] who have shown that the direct decomposition of ammonia sensitises the conversion of para hydrogen to ortho hydrogen.

The low overall quantum efficiency of the decomposition has been explained in two ways, neither of which is a complete solution of the kinetics of the reaction. The majority of workers have taken the view that the low quantum efficiency is due to recombination,

$$NH_2 + H + M \rightarrow NH_3 + M \ldots\ldots (3.),$$

and the work of Melville[6] in which the direct photo-decomposition of ammonia is inhibited by atomic hydrogen is prima facie evidence of such a recombination. But Farkas and Harteck[7] have repeated the ammonia sensitised para-ortho hydrogen conversions of Geib and Harteck and have found certain evidence which points to the hydrogen atom concentration being lower than is to be expected if the hydrogen atoms are removed by a third body process such as (3). It must be borne in mind, however, that the conditions of the two experi-

ments are quite different, the former being carried out at low pressures and the latter requiring a large excess of para hydrogen. Welge and Beckmann[8] have determined the quantum efficiency of the initial stages of the direct photodecomposition of ammonia and obtained the unexpected result that the quantum efficiency approaches unity and the nitrogen fraction of the products approaches zero as the decomposition approaches zero. This would also indicate that recombination (3) does not play an important part in the photodecomposition. Ammonia, however, is regenerated since Junger and Taylor[9] have shown that deuteroammonias are formed when ammonia is photodecomposed in the presence of atomic deuterium. Accordingly the source of regeneration has been sought in secondary reactions. In a flow system Gedye and Rideal[10] obtained yields of hydrazine from photodecomposed ammonia of as much as 57% of the stoichiometric yield by the equation,

$$2NH_3 \rightarrow N_2H_4 + H_2.$$

In static systems Koenig and Brings and, more recently, Welge and Beckmann have detected extremely small amounts of hydrazine. This evidence would seem to

indicate that hydrazine is formed in the initial stages and decomposed later. If, at high ammonia pressures and after the initial stages of the photodecomposition, hydrazine is formed more in the gas phase than at low pressures where combination of the amine radicals probably takes place, ammonia may be regenerated by the reaction of atmmic hydrogen with hydrazine. Mund and van Tiggelen[12] have developed this hypothesis to explain the kinetics of the ammonia photodecomposition with fair success. The reaction mechanism they suggest is as follows

		Relative Rate
1.	$NH_3 + h\nu \rightarrow NH_2 + H$	20
2.	$H + H + M \rightarrow H_2 + M$	2
3.	$2NH_2 + M \rightarrow N_2H_4 + M$	17
4.	$H + N_2H_4 \rightarrow NH_3 + NH_2$	16
5.	$N_2H_4 + 2NH_2 \rightarrow 2N_2 + 4H_2$	1

It accounts for nitrogen production being delayed to the later stages of the photodecomposition by (3), for the quantum efficiency becoming less than unity after the initial stages by (4) and quantitatively for the quantum efficiency being 0.2 at 1 atmosphere if the

relative rates are as given alongside the reaction scheme. The pressure and light intensity dependence of the quantum efficiency as determined by Wiig[13.] (also Ogg, Leighton and Bergstrom)[14.] and Mund,[15.] respectively, is predictable on the same grounds. But it is not an unique solution since Leighton[16.] has proposed a similar scheme in which reaction (5) becomes

5a. $N_2H_4 + 2NH_2 \rightarrow 2NH_3 + N_2 + H_2$

and the relative rates are 10: 2: 7: 6: 1.

It is on the kinetics of the photodecomposition of hydrazine that the Mund-van Tiggelen[12.] hypthesis stands or falls and these have not been studied to the same extent as those of ammonia. The absorption spectrum[2.] of hydrazine is diffuse like that of ammonia in the region 2490-2250°A where it becomes continuous to below 2000°A. Two possible primary processes of dissociation are indicated by this predissociation spectrum,

1. $N_2H_4 + h\nu \rightarrow N_2H_3 + H$

2. $N_2H_4 + h\nu \rightarrow NH_2 + NH_2$

No distinction has yet been made. In the present thesis a distinction has been attempted.

The overall reaction has been studied by Elgin and Taylor[17] who give the decomposition as

$$2N_2H_4 \rightarrow 2NH_3 + N_2 + H_2.$$

But Wenner and Beckmann,[18] using the same methods as Welge and Beckmann[8] employed in investigating the ammonia photodecomposition, report the non-condensable products as 58-64% hydrogen in the pressure range 14-2 m.m. hydrazine. The quantum efficiency in the same hydrazine pressure range is reported 1.7-1.0.

Reaction (4) in the Mund-van Tiggelen reaction mechanism is vital to the hypothesis. Ogg, Leighton and Bergstrom[14] have shown that when mixtures of ammonia and hydrazine are exposed to a zinc spark source of radiation only hydrazine decomposes, even though hydrazine absorbs only a small fraction of the radiation. The mechanism suggested is

$$1.\ NH_3 + h\nu \rightarrow NH_2 + H$$

$$2.\ H + N_2H_4 \rightarrow NH_3 + NH_2$$

The quantum efficiency based on total quanta absorbed is given as 1.28 and thus a reaction between amine radicals and ammonia must follow. Dixon[19] has investigated the reaction of atomic hydrogen with hydrazine in

a flow system and has shown the formation of ammonia. Though his results are often taken to indicate a very rapid reaction between atomic hydrogen and hydrazine there is no quantitative measure of the rate in them.

The purpose of the present thesis is to describe by new techniques the bearing on the Mund-van Tiggelen mechanism for the ammonia photodecomposition of the quantum and collision efficiencies of the reaction of atomic hydrogen with hydrazine, and of the general photochemical behaviour of hydrazine. This leads to a new and more satisfactory mechanism being proposed which is supported by quantitative data.

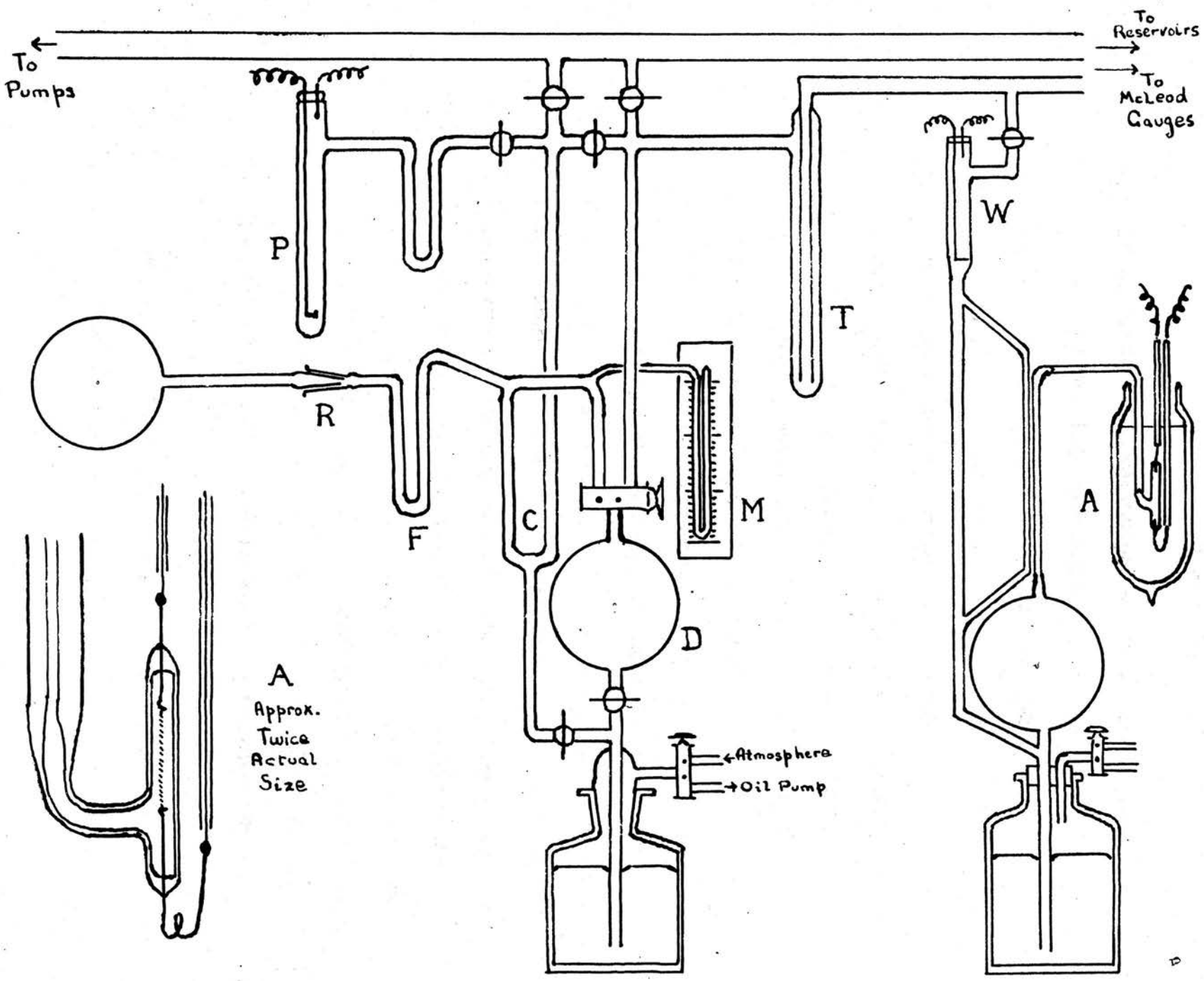


Fig. 1. General Diagram of Apparatus.

Apparatus.

The essentials of the apparatus are shown in Fig. 1. The whole system was constructed with soda glass. A glass three stage mercury diffusion pump, backed by a Hyvac rotary oil pump, was employed to evacuate the system. A liquid oxygen trap for condensable gases was inserted between the pumps. A vacuum better than 10^{-5} m. m. Hg could be attained and this was more than sufficient for the purposes of the present work. Fused silica reaction vessels could be attached at R by means of a ground joint. Since hydrazine is very readily absorbed in greases, the joint was sealed with Picene wax and a mercury cut-off C was used in place of a tap. A small U-tube F close to the reaction vessel was used to freeze out condensable gases by liquid oxygen. Pressures in the reaction vessels could be measured by the manometer M. The Toepler-doser arrangement D permitted of any suitable amount of gas being withdrawn from the reaction vessel for analysis. A further very valuable use of this arrangement was the speeding up of the freezing out of hydrazine from non-condensable gases. Despite its comparatively high freezing point, 1.4° C., hydrazine freezes out exceeding slowly from non-condensable

gases in a static system. However when mixtures of say 25% hydrazine in non-condensable gas were flowed through the U-tube F, cooled by liquid oxygen, by raising and lowering the mercury in D, hydrazine was removed completely by three or four movements. If a sample of the same mixture was withdrawn without previously removing the hydrazine and passed through the liquid oxygen trap T, hydrazine could be detected in a McLeod gauge on comparison with a control sampling without hydrazine. The data given in Table 1 is typical.

Table 1.

H_2 Pressure in Reaction Vessel	Hydrazine Pressure	McLeod Gauge Readings	Calculated Hydrogen Pressure
m.m.	m.m.		m.m.
51.0	-	72.0	-
52.3	-	74.1	-
49.9	13.3	81.0 78.7 78.2	55
48.8	13.0	77.0 76.0 72.0	54

When hydrazine was in the reaction vessel it was always removed by flowing the reaction mixture through the/

the cooled U-tube before carrying out any analyses. This procedure of flowing the reaction mixture was also useful when vapourising frozen hydrazine. To the reaction system were connected two Pirani gauges P and P', an oil gauge, two McLeod gauges and a micro-thermal conductivity analyser A in addition to the manometer M. The Pirani gauges were operated by the Campbell method,[45] the applied voltages being read by an Avometer. The linear relationship between pressure and $V^2-V'^2$ (where V is the voltage to be applied to maintain the standard temperature of the wire - .015 m.m. diameter platinum - at any pressure and V' is the voltage required at the lowest pressure attainable, viz. 10 m.m. held for hydrogen up to about 0.4 m.m. and to about 0.25 m.m. for nitrogen. The pressures measured by the gauges were well within these limits. In experiments where Pirani P' was used to measure the pressure of a non-condensable gas from which had been frozen out a condensable gas, particularly hydrazine, the U-tube trap was cooled with liquid oxygen to remove any remaining condensable gas. If this trap were not inserted the time required to obtain a steady reading on the Pirani was unduly long/

long. One of the McLeod gauges read up to 0.18 m.m., while the other read to 0.7 m.m. Considering the very different sensitivities the two gauges agreed fairly well. The oil gauge was filled with Apiezon oil B. It was used only for approximate measurements of low para-hydrogen pressures.

For analysis of mixtures of hydrogen-nitrogen, ortho-para hydrogen, and ortho-para hydrogen-nitrogen the microthermal conductivity method developed by Bolland and Melville[20] was used. The design of the micro-pirani gauge is slightly modified for ease of construction (Fig. 1). A coiled tungsten filament, supplied by the G.E.C. Ltd., was spot welded to .015 inch diameter platinum wire and then sealed into a short piece of capillary tubing of 2 m.m. bore and 1 m.m. walls. This tube had previously been sealed to thick walled capillary which, in turn, was sealed to 2 m.m. bore thin walled capillary tubing attached to the bulb of a McLeod gauge. The spiral of tungsten wire was about 0.1 m.m. in diameter, the diameter of the wire itself about 0.01 m.m. and the length of the spiral about 1.0 cm. The resistance of this length of spiral was 24.5 ohms at room temperature and 6.66 ohms at 93° K. The

gauge/

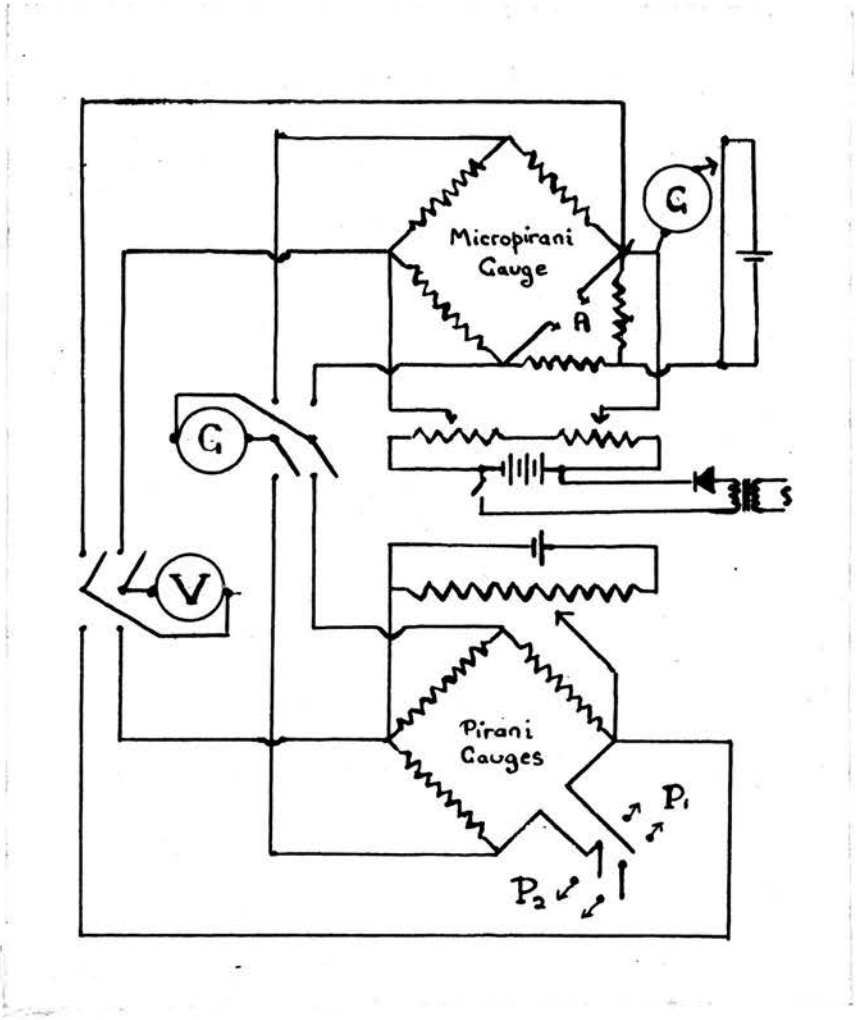


Fig. 2. Diagram of Electrical Circuits

gauge was operated by measuring, by means of a potentiometer, the voltage to be applied across the spiral to maintain it at 200°K (i.e. 16.0 ohms), while immersed in liquid oxygen. The pressure of the gases being analysed was always 50 m.m. which corresponds to a volume of $4.9\text{-}10^{-2}$ c.c. at N. T.P. At 50 m.m. the pressure dependence of the applied voltage is quite small, an error of 0.5 m.m. changing the applied voltage ca. 0.0005 V. The circuit (Fig. 2) consisted essentially of a Wheatstone bridge the arms of which were adjusted to balance when the resistance of the spiral was the value calculated for it at 200°K. The resistance of the spiral used was such that four volts across the bridge was sufficient even for 70% parahydrogen. This was obtained from three two volt cells in series. The success of this method of analysis depends to a certain extent on the constancy of the potential applied to the balanced circuit since it is extremely difficult to determine the potential across the spiral filament if it is at all variable. The cells proved very satisfactory in this respect. Since the drain on them was considerable a trickle charger was employed to keep them charged. The voltage applied

across/

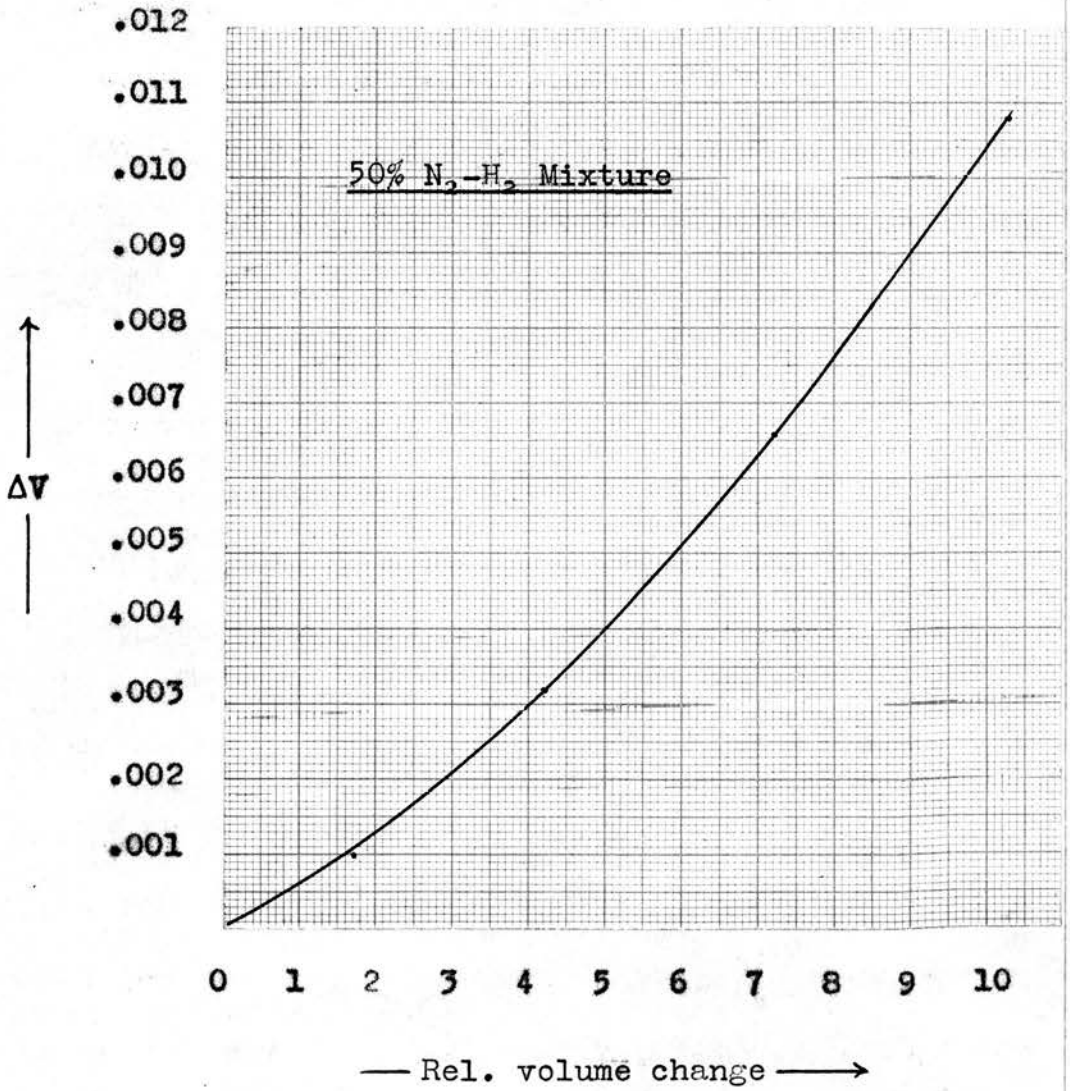


Fig. 3. Graph showing the variation in voltage accompanying change in volume of H_2 and N_2 in the micropirani gauge.

across the spiral was greater than this and thus it was necessary to shunt the spiral by a high resistance (11,700 ohms.) from which a potential within the range of the potentiometer could be tapped off.

When used to analyse hydrogen-nitrogen mixtures, the micropirani gauge was calibrated with known mixtures of these gases. The mixtures were made up at low pressures by means of the Pirani gauge in a bulb of large volume (500 c.c.) attached at R. At first difficulty was experienced in getting reproducible results. This was traced to two causes, one being a marked tendency of hydrogen to separate from the mixture and enter the micropirani gauge first when transferring the mixture, and the other an effusion effect in the gauge itself which imposes a volume dependence on the applied voltage. The first difficulty was overcome by allowing ample time (two or three minutes) for rediffusion at every stage of the transfer to the micropirani. By using a large volume for mixing only two displacements of the mercury in the Toepler-Doser arrangement were required at the most to transfer the mixture to the micropirani gauge. The second difficulty, which is shown graphically in Fig. 3, was overcome/

overcome by adjusting the hydrogen-nitrogen mixtures to the same initial pressure, before compression, in the micropirani by means of the Toepler-doser arrangement. Since there was no quick way of measuring the initial pressure, resulting deviations from the standard calibration volume were corrected by the volume-voltage dependence curves. The effusion effect was appreciable only in 25%-75% nitrogen mixtures. A detailed interpretation of the data is a matter of extreme difficulty owing to the inherent complexity of this effect.

When the micropirani was used to analyse hydrogen with a para content above the normal equilibrium value of 25% the applied voltages at pressures from 150 m.m. to 200 m.m. were determined and extrapolated to infinite pressure by the relation

$$1/V_\infty^2 = 1/V^2 - C/p \ldots (1)$$

where C is a constant. Typical data is given in Tables 2a and b.

Table 2a.

Normal hydrogen

Volt	$1/V^2$	p	1/p

Volt	$1/V^2$	p	1/p
		m.m.	
1.6873	0.3514	150	0.00667
1.6882	0.3510	160	0.00625
1.6892	0.3505	170	0.00588
1.6903	0.3500	180	0.00556
1.6907	0.3499	190	0.00526
1.6914	0.3495	200	0.00500

C = 1.116

Table 2b.

Para hydrogen

Volt	$1/V^2$	p	1/p
		m.m.	
1.7736	0.3179	200	0.00500
1.7730	0.3182	190	0.00526
1.7723	0.3184	180	0.00556
1.7691	0.3196	150	0.00667

C = 0.9928

From (1) $\frac{V^2_{\infty\ p\text{-}H_2}}{V^2_{\infty\ o\text{-}H_2}} = \frac{0.3439}{0.3129} = 1.100.$

From the data of Bolland and Melville[20] this corresponds to a para content of 77%. The pressure of oxygen over the liquid in the pumped out Dewar vessel round the charcoal, on which the para hydrogen was prepared, was 10 m.m. Hg. which corresponds to 60° K (I.C.T. 3,203). From the data of Farkas for the para-orthohydrogen equilibrium over charcoal at this temperature the para hydrogen content is 65%. The discrepancy/

discrepancy between these values is rather large but it was decided to take the mean, the error thus introduced into subsequent calculations being small. Since the usual method of ternary analysis by working at two wire temperatures (Bolland and Melville) requires frequent and rather laborious calibrations of the micropirani, a special method was evolved to analyse para-ortho-hydrogen-nitrogen mixtures. The voltage (V_{p-H_2}) applied to the micropirani gauge with a mixture of non equilibrium hydrogen and nitrogen was measured, the hydrogen equilibrated at low pressure by a glowing platinum wire and the voltage (V_{Equil}) applied again measured. Since $V_{p-H_2}-V_{equil}$ is not a true measure of the para hydrogen content in the non-equilibrium hydrogen when nitrogen is present a correction factor V_{n-H_2}/V_{equil} was applied. The theoretical basis for this correction is as follows.

In the absence of nitrogen the heat loss by the spiral wire can be expressed by

$$kV^2 = b\,K_{p-H_2} + (1-b)\,K_{o-H_2}$$

where V is the voltage applied across the spiral, b is the fraction of para hydrogen and K_{p-H_2}, K_{o-H_2} are the thermal/

thermal conductivities of para and ortho hydrogen. The change in applied voltage with change in the para hydrogen fraction is

$$\frac{dV}{db} = \frac{2\,kV}{K_{p-H_2} - K_{o-H_2}}$$

Similarly in presence of nitrogen the heat loss of the spiral is

$$kV^2_{N_2} = dK_{N_2} + bK_{p-H_2} + (1-b)\,K_{o-H_2}$$

and $$\frac{dV_{N_2}}{db} = \frac{2kV_{N_2}}{K_{p-H_2} - K_{o-H_2}}$$

If db is the same in both cases, then

$$dV = \frac{V}{V_{N_2}}\, dV_{N_2}$$

Table 3 shows the good agreement between the computed and observed values of dV for para hydrogen in presence of nitrogen.

Table 3.

Analysis of Para Hydrogen in Presence of Nitrogen.

Nitrogen	Analysis Voltage	Voltage after Equilibration	ΔV_{p-H_2}	$\Delta V_{p-H_2} \times \frac{V}{V_{equil}}$
-	1.7750	1.7151	0.0599	0.0599
2%	1.7485	1.6858	0.0594	0.0604
5%	1.7131	1.6563	0.0568	0.0588
8%	1.6652	1.6093	0.0559	0.0595
12%	1.6246	1.5701	0.0513	0.0560

The correction for N_2 was taken to hold up to 10% N_2 which/

which was never exceeded in any of the experiments where this correction was used.

Difficulty was experienced with the equilibration due to degassing of the glowing wire. Originally a nickel wire was used and it was found that pure non-equilibrium hydrogen when equilibrated gave a voltage value well below that of normal hydrogen. Even after 5-6 hours of baking at cherry red head in vacuo, hydrogen equilibrated on the wire gave voltage values 0.003 volts lower than normal hydrogen. The prolonged baking frequently rendered the wire inactive and the subsequent activation by oxidation and reduction made a further period of degassing necessary. That degassing was the cause of the low equilibration voltage values and not impurity of the non-equilibrium hydrogen was definitely established by control experiments with normal hydrogen. Since it seemed likely that the gas in the nickel wire was carbon monoxide, residual from its preparation from nickel carbonyl, a platinum wire was substituted. Except for the fact that the platinum was not so easily poisoned there was no appreciable improvement. In daily use, the wire was baked in vacuo for two or three hours and in this way the correction limited to +0.0015 to +0.0025 volts when the wire

was/

was glowing at a cherry red heat for five minutes. At this wire temperature equilibration was always complete in five minutes.

Preparation of Gases.

Hydrazine.

Liquid hydrazine was prepared by distilling commercial 50% hydrazine hydrate in vacuo several times over potassium hydroxide. The distillation system consisted of a boiler flask connected through a water cooled condenser to a receiver. Between the receiver and the condenser was inserted a vacuum triangle which permitted of evacuating either both the flask and the receiver or each separately by the pumps of the main apparatus. Glass to glass connections were used throughout, the flask and receiver being detachable by ground joints. The minimum of grease was used on these joints and the taps of the vacuum triangle. After each distillation the potassium hydroxide was renewed in the flask. Further distillations were carried out over potassium hydroxide in vacuo at low temperature, by alternately cooling connected tubes containing potassium hydroxide/

hydroxide with liquid oxygen. In this way hydrazine was obtained which, when decomposed on a nickel wire at about 900° C., gave an analysis of 34% N_2 by the micro-thermal conductivity method described later. The hydrazine was stored over potassium hydroxide in vacuo. Over periods of 24 hours or so, slight decomposition to non-condensable gas was frequently observed. Before using hydrazine in experiments the reservoir was opened to the pumps for a few minutes. After being introduced into the reaction vessel, hydrazine was frozen out, generally with liquid oxygen, and any residual non-condensable gas was pumped off. When carbon dioxide and ether mixtures were used to freeze out, no ammonia was detectable on the manometer.

Ammonia.

Commercial cylinder ammonia was used after purification by fractional distillation with liquid oxygen.

Hydrogen.

Hydrogen obtained from cylinders was purified of traces of oxygen by passing it over palladised asbestos at 300°C and then through a liquid oxygen trap.

para-Hydrogen.

para-Hydrogen was prepared by absorbing hydrogen in/

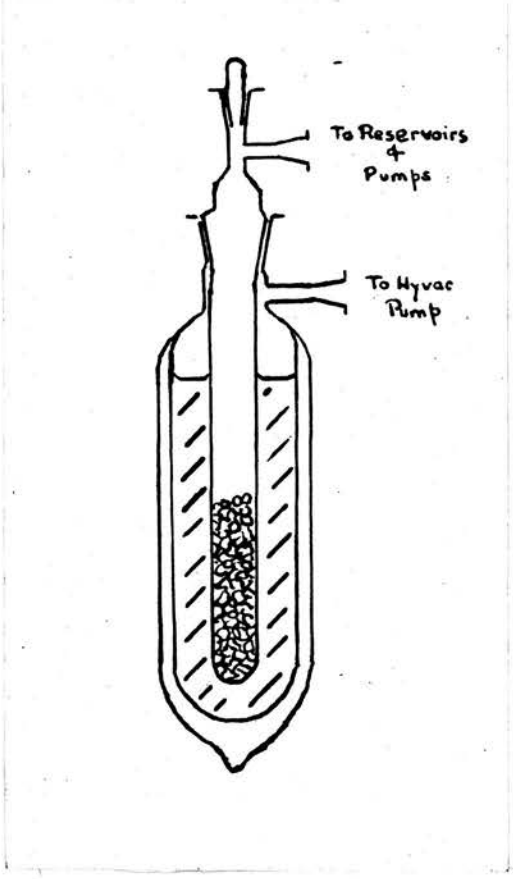


Fig. 4. Apparatus for the preparation of para hydrogen.

in liquid oxygen cooled animal charcoal, previously baked in vacuo. Since the para-hydrogen content increases to only about 50% at the temperature of liquid oxygen the vapour over the liquid was pumped off by a hyvac pump to reduce the temperature. The apparatus is shown in Fig. 4. At the best the oxygen vapour pressure could be reduced to 10 m.m. From the micro-thermal method of analysis and the data of Bolland and Melville the para-hydrogen content of the hydrogen so treated was generally computed about 70%. The pressure of hydrogen over the charcoal was about 500 m.m. and the gas was kept on the charcoal about an hour. The first fraction of hydrogen was drawn from the charcoal by means of a Toepler pump. The remaining hydrogen was obtained from the charcoal by allowing it to come slowly to a higher temperature by stopping the pumping and then removing the liquid oxygen. The first fraction usually contained 10% para-hydrogen more than the second.

Nitrogen.

Cylinder nitrogen was passed over reduced copper turnings at 300 C. to remove traces of oxygen. Any condensable gases were removed by passing through a liquid oxygen trap.

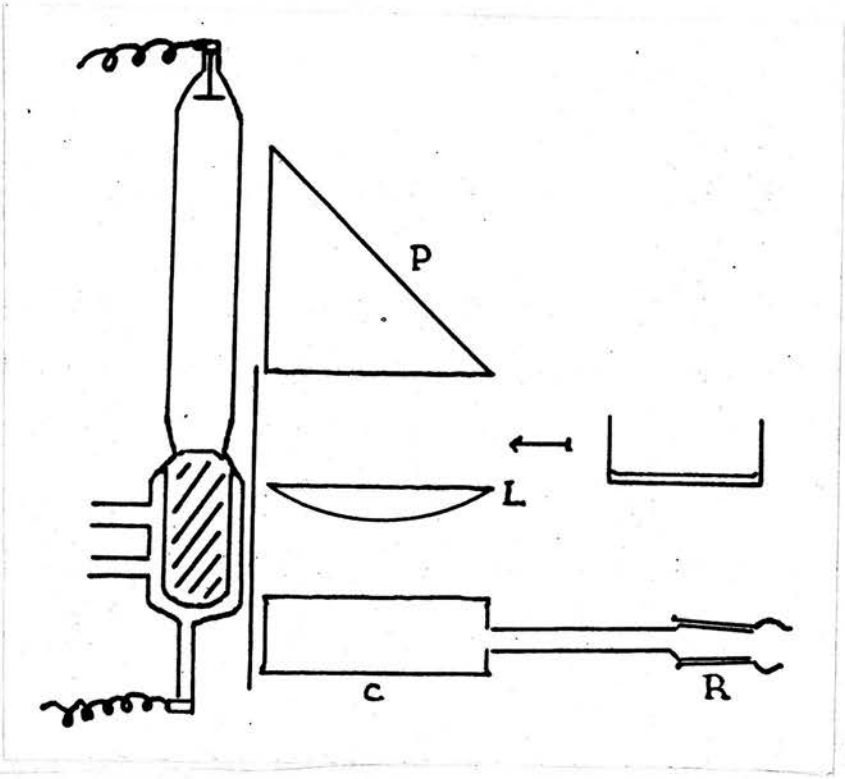


Fig. 1. Diagram of the Optical Arrangement.

Quantum Efficiency of the Reaction of Atomic Hydrogen with Hydrazine.

Since the quantum efficiency of the reaction (4) of the Mund-van Tigglelen mechanism for the decomposition of ammonia (page 12)

$$H + N_2H_4 \rightarrow NH_3 + NH_2$$

has been determined only indirectly by Ogg, Leighton and Bergstrom[14] (vide pages 14 and 12), a direct determination has been made.

The essentials of the reaction system and the optical arrangements are given in Fig. (1).
The reaction vessel C consists of a plane ended cylindrical silica cell, 6 cms. in diameter and 2 cms. deep. Atomic hydrogen was produced in the cell by mercury sensitised photodecomposition of molecular hydrogen. A small drop of clean mercury was introduced into the cell to ensure that mercury vapour was always present. The source of the 2537°A wavelength to excite the mercury resonance line of that wavelength was a mercury arc discharge lamp A which was

run off a 100 volt D.C. supply through a large capacity choke. The cathode was water cooled and it was found necessary to keep the temperature of this water fairly constant if the quantum output of the lamp was to remain constant. Since the design of the lamp did not permit of it being used in the horizontal plane, and since a liquid actinometer, the uranyl oxalate actinometer, was employed to measure the 2537°A quantum input, a fused quartz prism P had to be introduced to deflect the light upon the cell C. The lens L caused the light to converge as it passed through the cell; the focal point lay beneath the cell.

The uranyl oxalate actinometer solution, used to measure the quantum input, was .005M and .0025M with respect to uranyl oxalate and oxalic acid, respectively. These concentrations are recommended by Forbes and Heidt.[24] The period of illumination was always limited to give not more than a 10% decomposition of oxalic acid, which is stated by these authors to be the limit of the desirable change in concentration. The amount of decomposition was measured volumetrically by 1/100N $KMnO_4$.

In order to avoid unduly long exposures of the

uranyl actinometer solutions, a semi-micro method was developed. The total quanta entering the cell C were first determined in the usual manner by completely filling the cell with actinometer solution and determining the normality decrease after an hour exposure. Immediately before and after these exposures, pipetted 2 ml portions of the actinometer solution were exposed for 5 minutes in small crystallising dishes above the lens L and the normality decrease in them determined by titration with the $KMnO_4$ solution run from a 5ml burette. Since variation in the amount (1 ml) of H_2SO_4, added for titration, might be of importance with such small titrations, this was added from a 2 ml. burette. This acid was used to wash the last traces of actinometer solution from the dish to a 25 ml. conical flask. In subsequent determinations of the quantum input, it was necessary to expose only a 2 ml. portion of actinometer solution above the lens when any variation from the originally measured total quantum input could be detected. Table (1) shows the constant relation between the total quantum input, measured by actinometer solution in the cell, and the decomposition of the actinometer solution in the 2 ml. portions above

the lens. The results given were over a period of weeks.

Table (1).

Total Quanta	$\frac{d[HCOOH]}{dt}$ in 2 ml. portion	Ratio
$1.3\ 10^{18}$	0.54	.241
$1.1\ 10^{18}$	0.44	.250
$1.3\ 10^{18}$	0.54	.241
hv/min	mls. 0.01N $KMnO_4$	

Since the uranyl actinometer is sensitive to light of wavelength up to 4500°A, it was necessary to determine the 2537°A fraction of the radiation from the lamp. This was done by filtering the light from the lamp through a 50% solution of acetic acid in water in a rectangular filter cell, which cuts out light of $\lambda < 2270$°A, and then determining its output above 2270°A by the actinometer. Another determination was then made with carbon tetrachloride in the filter cell, thus obtaining the output of radiation with a $\lambda < 4500$°A and $\lambda > 2537$°A since carbon tetrachloride cuts off 99.9% of the mercury resonance line 2537°A, but owing to its rapidly diminishing extinction coefficient, permits of the passage of the strong lines of longer wavelength, e.g. 3030°A (Melville and Walls)[22]. By sub-

tracting the latter determination of output from the former, the 2537°A output was found to be 39% of the total radiation, a mean of two concordant results, 38% and 40% separated by a period of weeks.

In order to determine the amount of 2537°A radiation absorbed by the mercury vapour in the cell, actinometer solution was exposed beneath the evacuated cell and the light falling upon it filtered through 50% acetic acid solution in a filter cell. Carbon tetrachloride was substituted for the acetic acid and a further exposure made. A typical result is given below in Table (2).

Table (2).

Filtered Exposures of Actinometric Solution beneath Cell.

Exposure Time mins.	Filter	Cell	Normality Decrease mls. 0.01 N/$KMnO_4$
8	CCl_4	Hg	0.24
8	CCl_4	Hg + 50 m.m. H_2	0.24
8	CH_3COOH	Hg	0.25

Thus absorption of 2537°A is 100%.

The method adopted to measure the number of molecules of hydrazine decomposed was to determine the in-

crease in non-condensable gas pressure. The number of molecules decomposed was calculated on the assumption that atomic hydrogen reacts with hydrazine according to the stoichiometric equation,

$$H + N_2H_4 = NH_3 + \tfrac{1}{2}N_2 + H_2$$

Analyses of the hydrogen-nitrogen ratio are given in the next section. About 10 m.m. of N_2H_4 was introduced into the cell and frozen out with a mixture of CO_2 and ether or liquid oxygen on the U-tube F (Fig. 1, Apparatus Section). After pumping off any traces of non-condensable gas, about 50 m.m. of H_2 were introduced and the pressure measured accurately. A measured dose was withdrawn from the rection cell in the Toepler-doser arrangement and passed to a McLeod gauge where the resulting pressure was measured. The withdrawal of a few doses in this manner served to establish a relation between the pressure in the cell and the resulting pressure in the McLeod gauge, allowance being made, by direct manometric measurement, of the decrease of pressure in the cell due to withdrawal of the doses. The hydrazine was vapourised by flowing the hydrogen through the U-tube F by displacement of the mercury in the Toepler-doser and the reaction cell illuminated with the

mercury vapour lamp radiation. After exposure, the hydrazine was frozen out in the liquid oxygen cooled U-tube trap F by the same method of flowing in the gases. The increase in pressure of the non-condensable gas produced was measured by withdrawing a dose of the same volume as before and measuring the resulting pressure in the McLeod gauge. In order to measure the amount of ammonia produced, the non-condensable gases were pumped off and a mixture of CO_2 snow and ether applied to the U-tube F. At the temperature of the mixture (ca. -80° C.), the vapour pressure of hydrazine is of the order 10^{-2} -10^{-3} m.m. Since ammonia has a vapour pressure of 33 m.m. at this temperature, the amount of ammonia produced, less than 5 m.m. always, could be determined on a mercury manometer.

The results of a number of determinations of the quantum efficiency of the reaction of atomic hydrogen with hydrazine are summarised in Table (3).

Table 3. Quantum Efficiency of H-atom Sensitised Decomposition of N_2H_4.

Vol. 61 c.c. Temp. 20° C.

$p_{N_2H_4}$ m.m.	p_{H_2} m.m.	Exposure Times min.	Δp(n.c.)	Δp/min.	p_{NH_3} m.m.	mols. NH_3 / mols. N_2H_4	Total hv/min.	γ
10.7	47.6	5	0.6	0.12	-	-	$1.3.10^{18}$	
		+ 5	0.6	0.12	-	-	"	
		+ 5	4.6	0.09	3.6	0.66	"	0.46
12.7	50.0	10	0.8	0.08	-	-	$1.2.10^{18}$	
		+ 10	1.6	0.16	-	-	"	
		+ 10	1.5	0.15	-	-	"	
		+ 10	1.0	0.10	2.0	0.42	"	0.51
12.1	51.1	10	0.9	0.09	-	-	$1.3.10^{18}$	
(liq. N_2H_4)		+ 10	1.3	0.13	-	-	"	
		+ 10	0.8	0.08	-	-	"	
		+ 20	2.0	0.10	2.3	0.46	"	0.40
12.1	50.7	20	1.6	0.08				
		+ 20	1.5	0.08				
		+ 20	2.1	0.11	3.0	0.56	$1.3.10^{18}$	0.35
			Doser loss 1.3 mm/dose			Mean 0.52		Mean 0.43

In performing these experiments, there is a complication due to the mercury sensitised decomposition of hydrazine. In order to compute the magnitude of this reaction accurately, it would be necessary to know the quenching radius of hydrazine. This has not been measured, but for the purposes of argument, a very large value may be taken, namely 5.10^{-8} cm. The value for hydrogen is $2.45\ 10^{-8}$ cm. (Zemanski)[33]. Now the fraction of mercury atoms deactivated by hydrogen will be given by the formula

$$f_{H_2} = \frac{\sigma^2_{H_2}\left(\frac{1}{M_{Hg}} + \frac{1}{M_{H_2}}\right)^{\frac{1}{2}} p_{H_2}}{p_{H_2}\sigma^2_{H_2}\left(\frac{1}{M_{Hg}} + \frac{1}{M_{H_2}}\right)^{\frac{1}{2}} + p_{N_2H_4}\sigma_{N_2H_4}\left(\frac{1}{M_{Hg}} + \frac{1}{M_{N_2H_4}}\right)^{\frac{1}{2}}}$$

Inserting the above values and taking the hydrogen pressure as 50 m.m. and that of hydrazine 10 m.m., then

$$= \frac{6.0 \times 10^{-16}\ \left(\frac{1}{200} + \frac{1}{2}\right)^{\frac{1}{2}} \times 50}{50.60.10^{-16}\left(\frac{1}{200} + \frac{1}{2}\right)^{\frac{1}{2}} + 10.25.10^{-16}\left(\frac{1}{200} + \frac{1}{32}\right)^{\frac{1}{2}}}$$

$$= \frac{2.13.10^{-14}}{2.13.10^{-14} + 4.76.10^{-15}}$$

$$= 0.82$$

It will be seen therefore that the extent of the mercury sensitised hydrazine decomposition can practically be neglected in the discussion of the mechanism of the reaction.

In the reaction of atomic hydrogen with hydrazine there are two possible primary reactions

$$H + N_2H_4 = NH_3 + NH_2 \quad \ldots\ldots\ldots\ldots (1)$$

and $$H + N_2H_4 = N_2H_3 + H_2 \quad \ldots\ldots\ldots\ldots (2)$$

It is, however, improbable that the second reaction, i.e. dehydrogenation, occurs, since in the reaction of atomic hydrogen with ammonia, exchange occurs without any heat of dehydrogenation. This view is also supported by experiments on the reaction of atomic hydrogen with methane and with ethane. With the former molecule dehydrogenation takes place[24] thus

$$H + CH_4 = CH_3 + H_2$$

and no true exchange can be detected. Now with ethane, there are again two possibilities, as with hydrazine. But in spite of the fact that dehydrogenation could occur, the ethane molecule[46] is attacked at the C-C bond and broken up into CH_4 and CH_3. From this analogy therefore, it may be provisionally concluded that the attack of atomic hydrogen on hydrazine results in the primary production of ammonia and an amine radical (1). If it is supposed that the amine radicals then decompose to form nitrogen and hydrogen (vide page 133), it would be expected that the quantum efficiency of the whole process would be 2.

It will be observed, however, from Table (3) that (a) the quantum efficiency is only 0.4 and that (b) the number of ammonia molecules produced is considerably less than the number of molecules of hydrazine decomposed. These numbers, of course, ought to be identical since one ammonia molecule is produced for each hydrazine molecule decomposed according to (1).

There are four possible explanations of these facts. The first is that the excited mercury atom produces only one hydrogen atom and a Hg H complex molecule, the latter not reacting effectively with the hydrazine owing, for example, to the higher energy of activation. This will reduce the quantum efficiency by a factor of two. The second but less probable explanation is that a fraction of the hydrogen atoms combine without reacting with the hydrazine. Now it will be shown later that the energy of activation of the above reaction is 6850 cals (page 70); also the quantum efficiency for the para-orthohydrogen conversion at pressures of the order of 50 m.m. is about 10-15 which means that the probability of a hydrogen atom exchanging with a hydrogen molecule is 10-15 times that of its combining with another atom. Since the energy of this exchange reaction is also 7000 cals, the pro-

bability of a hydrogen atom reacting with hydrazine will be about 10-15 times that of its combining. However, these explanations do not account for the abnormally small amount of ammonia formed. This suggests that a fraction of the amine radicals reform hydrazine, while the remainder decompose to nitrogen and hydrogen. This would suggest a plausible explanation of the low quantum efficiency. It may be noted here that there already exists some evidence (Gedye & Rideal)[10] to indicate that amine radicals do combine to give appreciable quantities of hydrazine. At present it is not possible to find which is the correct explanation.

In computing the 2537°A quanta from the decomposition of oxalic acid in the uranyl oxalate actinometer, the value of 0.6 for the quantum efficiency was employed in accordance with Forbes and Heidt.[21] With regard to this value, it is worth mentioning that comparison of the monochloracetic acid hydrolysis actinometer with the uranyl oxalate actinometer has shown that the radiation intensity values obtained from the former are approximately half those from the latter; the quantum efficiency of the monochloracetic acid

hydrolysis is taken as unity for 2537°A in accordance with Rudberg.[25] This factor of two between intensity values measured by these actinometers has been observed by Farkas & Melville[24] and Leighton, and Smith & Leighton.[26] The latter authors, however, were satisfied with the value of 0.6 for the quantum efficiency of the uranyl oxalate actinometer and the former had no standard of comparison. But Bolland & Melville[27] have used the uranyl oxalate actinometer to measure the quantum efficiency of the mercury sensitised decomposition of phosphine and find the value so computed about half that obtained by an independent back reaction technique. This technique gave identical values for the mercury sensitised and direct decompositions of phosphine, that of the latter being in good agreement with a more direct measurement by Melville,[28] using ammonia as an actinometer. In view of this evidence of such a large factor as two of discrepancy in these liquid actinometers, their quantum efficiencies require to be investigated again thoroughly.

Collision Efficiency, Activation Energy and Steric Factor of the Reaction of Atomic Hydrogen with Hydrazine.

In order to obtain the number of effective collisions between hydrogen atoms and hydrazine

$$H + N_2H_4 \rightarrow NH_3 + NH_2 \ldots\ldots\ldots (1)$$

the stationary concentration of atomic hydrogen must be known accurately, together with the rate of disappearance of atomic hydrogen. The stationary hydrogen atom concentration may be computed if the rate of production and rate of removal of hydrogen atoms are known. The general expression for hydrogen atom concentration is therefore

$$\frac{d[H]}{dt} = f(I) - k_1[H][X] - k_2[H] = 0$$

where $f(I)$ is the rate of production as a function of the incident intensity I and the second and third terms represent the rate of removal of hydrogen atoms by (a) third body collision and by (b) processes such as diffusion to the walls and interaction with reducible molecules. When the third term is small

compared with the second, the concentration of atomic hydrogen can be computed since (I) can be measured photochemically and $k_1[x]$ is known from separate experiments. On the other hand if $k_2[H]$ is very much greater than $k_3[H][x]$ as occurs with hydrazine (vide infra), then this method is inapplicable and some other technique must be adopted.

The method which seems most desirable is to compare the stationary hydrogen atom concentration with that of a reaction where the reaction kinetics are well known and, preferably, one where the hydrogen atoms do not disappear in the course of the reaction. The para-ortho chain conversion of para hydrogen

$$H + p\text{-}H_2 \rightleftharpoons o\text{-}H_2 + H$$

satisfied these conditions adequately. There is still a certain amount of uncertainty about the absolute values in the kinetics of the conversion, but any error so introduced into the determination of stationary hydrogen atom concentrations can easily be adjusted once the kinetics are established definitely. The application of this method, however, is limited to reaction where the reactants and the products are not para-magnetic and thus do not bring about conversion

by themselves. When using this method to find the stationary hydrogen atom concentration in a reaction such as (1) above, it is necessary to measure only the rate of the para-ortho hydrogen conversion in presence of the photodecomposing substance and the concentration can be calculated from

$$[H] = 2.3 \log. 2 / t_{\frac{1}{2}} k^*$$

where $t_{\frac{1}{2}}$ is the half life of the conversion and k^* is the sum of the partial velocity constants k_a and k_b in the equation of the rate of conversion

$$d[p\text{-}H_2] / dt = k_a [H][p\text{-}H_2] - k_b [o\text{-}H_2][H]$$

where $p\text{-}H_2$ is the para hydrogen content and $o\text{-}H_2$ the ortho hydrogen content.

In the present series of experiments, use was made of this technique of measuring stationary hydrogen atom concentrations in determining the collision efficiency of the reaction of atomic hydrogen with hydrazine. It provides the only readily available means of determining this quantity, a knowledge of which is essential to the proof of the Mund-van Tiggelen mechanism for ammonia, (p. 12).

Atomic hydrogen was formed by the mercury sensitised photodissociation of molecular hydrogen

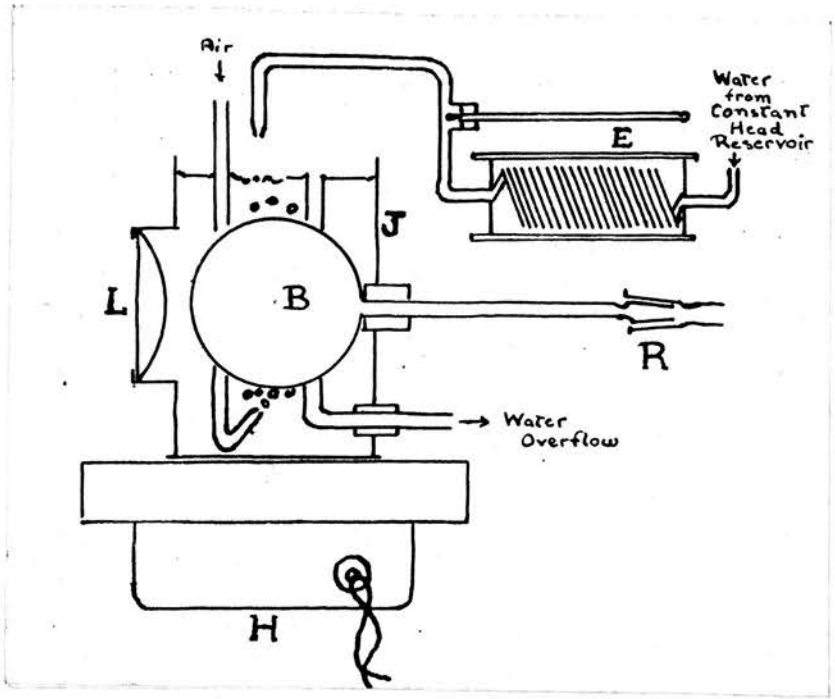


Fig. 1a. Reaction Vessel in Water Thermostat.

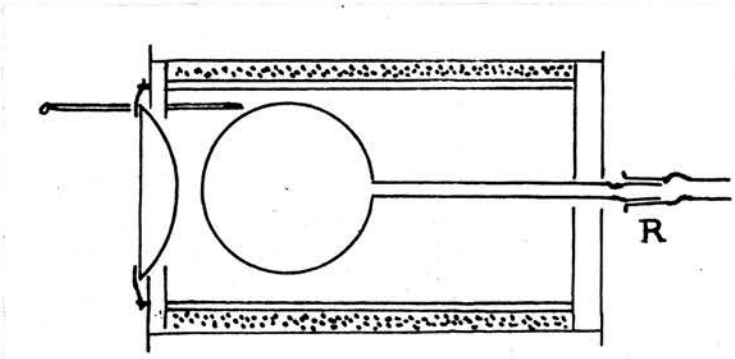


Fig. 1b. Reaction Vessel in Electric Furnace.

and the rate of para-ortho hydrogen conversion measured in the presence of the competing reaction of atomic hydrogen with hydrazine.

$$Hg + 2537h\nu \rightarrow Hg^*$$

$$Hg^* + H_2 \rightarrow H + H + Hg$$

$$H + H + M \rightarrow H_2 + M \quad \ldots\ldots (2)$$

$$H + p\text{-}H_2 \rightarrow o\text{-}H_2 + H \quad \ldots\ldots (3)$$

$$H + N_2H_4 \rightarrow NH_3 + \tfrac{1}{2}N_2 + H_2 \quad (4)$$

At the high pressures (50 m.m.) of para hydrogen employed the rate of conversion by recombination of the hydrogen atoms (2) is negligible compared with the conversion by the chain reaction. Thus only reactions (3) and (4) need be considered in the reacting system when computing the stationary hydrogen atom concentration from the rate of conversion.

The essentials of the reaction system are given in ~~this~~ Fig. (1). The reaction vessel consisted of a fused quartz bulb B 6.5 cms. in diameter and about 100 c.c. capacity. This was attached to the pumps and the gauges at the ground joint R in Fig. 1 of the Apparatus Section. The bulb was thermostated by a water jacket J to which was mounted by means of a screw fitting a lens L of fused quartz. Tap water was

fed into the jacket from a constant head reservoir through an electrically heated water furnace E. The water in the jacket was maintained at a constant height by an overflow tube. The temperature of the inflowing water could be regulated either by controlling the rate of flow through the furnace or by controlling the temperature of the furnace. It was easily possible to maintain the temperature constant to 1°C by manual control. In order to ensure the temperature of the water was uniform throughout the jacket, a stream of compressed air was passed through the water. When temperatures above 20-30°C were desired, the water flowing through the jacket was heated by a hot-plate H. The highest temperature which could be conveniently maintained in this way was about 95°C. A constancy of 1°C was again possible with a little more care. For temperatures above 100°C, it was necessary to employ an electrically heated reaction furnace (Fig. 1b) which consisted of an electrically heated silica core in a copper container. The same limit of variation in the temperature control could be maintained manually.

In order to measure the percentage of nitrogen in

the non-condensable gas produced in the reaction, the micropirani gauge required to be calibrated for mixtures of hydrogen and nitrogen in the manner described in the Apparatus Section (page 21).

The experimental procedure in a typical conversion run was as follows. The platinum wire used to equilibrate non-equilibrium para hydrogen (which will be called para hydrogen for convenience) was heated to approximately 900° C in vacuo for one to two hours in order to reduce the correction necessary for degassing to 0.0020 volt. (page 26 of Apparatus Section). The temperature of the thermostat was adjusted to the desired temperature, hydrazine introduced to 10 m.m. and frozen out in the U-tube F (~~Fig. 1~~). After pumping off any traces of non-condensable gas, para hydrogen was introduced to 50 m.m. At this point a few voltage values of the para hydrogen in the micropirani gauge were taken and each sample equilibrated to check the outgassing of the platinum wire. In this connection it is worth noting that the wire had to be isolated from the main vacuum line of the apparatus by a liquid oxygen trap, since hydrazine diffused from there to the wire despite the action of the pumps. Hydrazine is

very strongly adsorbed by the walls of the apparatus. Once the equilibration had been checked, the temperature of the thermostat and the pressure of para hydrogen in the reaction bulb were noted and a measured dose of para hydrogen passed to the McLeod gauge where the resulting pressure was observed. The procedure was the same in this respect as in the determination of the quantum efficiency of atomic hydrogen - hydrazine reaction (page 35). When the relation between the pressure in the reaction bulb and the resulting pressure in the McLeod gauge was established, the hydrazine was vapourised by the usual method of flowing the hydrogen through the U-tube. This was followed by a short exposure of the mixture of para hydrogen and hydrazine to the mercury vapour lamp. After exposure the hydrazine was frozen out by the usual flow method and the increase of pressure of the non-condensable gas measured by passing the same volume of gas to the McLeod as before. The dose was then expanded into the micropirani and its para hydrogen and nitrogen content determined by measuring its voltage value in the gauge before and after equilibration on the platinum wire (vide page 24). The hydrazine was vapourised

once more and the procedure repeated from that point until the total period of exposure was between 6 and 15 minutes. Either at the beginning or the end of the experiments the pressure decrease by withdrawal of the measured dose was determined accurately by observing the decrease that occurred on taking 6-7 doses from the reaction vessel. This decrease generally amounted to 1.0 m.m. per dose which is rather large but unavoidably so. The actual increase in non-condensable gas pressure generally was of the order of 2.0 m.m. on a two minute exposure to the lamp, thus the loss of pressure through the doser cut the observed increase by half. The time required to carry out this procedure for a conversion run involving five or six short exposures was from six to seven hours.

The data obtained from a series of these runs are grouped under various headings below.

Hydrogen-Nitrogen Ratio in Non-Condensable Gases. Produced by Reaction of Atomic Hydrogen with Hydrazine.

The hydrogen-nitrogen ratio in the non-condensable products was determined in only a few of the conversion runs. Two typical determinations are given in Table 1 a and b.

Table 1 a.

Temp. 20° C. Volume

Run	Press N_2H_4 m.m.	Press p-H_2 m.m.	Time min.	Reading on McLeod	Press n.c. Gas m.m.	Corrected P n.c. [+] m.m.	Δp n.c.	Corrected * Δp n.c.
I	6.1	51.1	0.0	137.2	51.1	51.1	-	-
			2.0	138.5	51.6	52.6	1.5	2.0
			4.0	139.5	52.0	54.0	2.9	3.9
			6.0	138.4	51.6	54.6	3.5	4.7
			8.0	138.8	51.7	55.7	4.6	6.1
			10.0	135.7	50.5	55.5	4.4	5.9
II	3.0	51.1	0.0	135.0	51.1	51.1	-	-
			2.0	136.9	51.8	53.1	2.0	2.7
			4.0	135.6	51.3	53.9	2.8	3.7
			6.0	133.0	50.4	54.3	3.2	4.3
			8.0	127.6	48.3	53.5	2.4	3.2
			10.0	124.6	47.2	53.7	2.6	3.5

[+] Doserlosses I 1.0 m.m./dose II 1.3 m.m./dose.

* Multiplied by 4/3 to account for hydrogen atoms disappearing by reaction with hydrazine.

Table 1 b.

V_{N_2} = 0.7068 V

Run	Time	Eq. Volt[+]	$V_{eq}^2 - V_{N_2}^2$	$\%N_2$	m.m.N_2	$\%N_2$ in Δp n.c.
I	0.0	1.7809	2.672	-	-	-
	2.0	1.7700	2.633	1.0	.51	25
	4.0	1.7474	2.554	2.5	1.3	33
	6.0	1.7246	2.475	4.5	2.3	49
	8.0	1.7066	2.413	5.8	3.0	50
	10.0	1.6977	2.382	6.5	3.3	56
II	0.0	1.7806	2.671	-	-	-
	2.0	1.7682	2.616	1.5	0.8	30
	4.0	1.7444	2.543	3.0	1.6	43
	6.0	1.7367	2.516	3.5	1.8	42
	8.0	1.7366	2.516	3.5	1.7	53
	10.0	1.7368	2.516	3.5	1.7	50

[+] Includes wire correction of 0.002 V.

The fraction of nitrogen in the non-condensable gas formed in the decomposition tends to increase with increasing decomposition and, at the same time, the fraction is considerably larger than the suggested mechanism $H + N_2H_4 \rightarrow NH_3 + \frac{1}{2}N_2 + H_2$ would indicate. No theoretical significance, however, has been taken from these results since there is necessarily a large degree of uncertainty in the experimental procedure adopted. The tendency of the fraction to increase is very probably due to errors in correcting for losses

of non-condensable gas which would be cumulative. As regards the absolute value of the fraction, it will be observed that this is, in effect, a percentage of a percentage.

The importance of these results is qualitative rather than quantitative, in that they clearly show the formation of N_2 in the reduction of hydrazine by atomic hydrogen.

Thermal Decomposition of Hydrazine.

At room temperature hydrazine is perfectly stable and in the numerous experiments carried out with it in presence of para hydrogen at this temperature over periods of hours, conversion of the latter was never detected. But before carrying out experiments on the inhibiting effect of hydrazine on the para hydrogen conversion at high temperatures, the rate of thermal decomposition of hydrazine and its influence on the para hydrogen conversion had to be determined. The thermal decomposition of hydrazine, shown in Table (2), was measured by introducing hydrazine into the reaction vessel, heated to the desired temperature, and observing the amount of non-dondensable gas produced on a Pirani gauge. The influence of the thermal decompo-

sition of hydrazine on para hydrogen was observed in a similar manner (Table 3).

Table 2.

Temp.	$p_{N_2H_4}$ m.m.	Time	p.n.c. gas m.m.	% Decomposition
75°C	8.0	15 mins.	0.002	.03%
100°C	8.0	15 mins.	0.006	.09%
218°C	9.0	15 mins.	0.500	5.6%

Table 3.

Temp.	$p_{N_2H_4}$ m.m.	$p_{p\text{-}H_2}$ m.m.	Time mins.	$\Delta V_{p\text{-}H_2}$	$\%\ p\text{-}H_2$	Conversion % p-H₂
100°C	12	53	0.0	.0694	62.1	
			15.0	.0692	62.0	0.1
200°C	9	50	0.0	.0694	62.1	
			15.0	.0673	61.0	1.1

Even at 200 C, the rate of thermal decomposition is very small and the apparent conversion of para hydrogen is due to this small amount of nitrogen and normal hydrogen produced. Correcting for the latter, the conversion becomes 0.5% which, if the data were available to correct for nitrogen, would reduce to the order of the experimental error of about 0.2%. Since hydrazine was never in contact with para hydrogen as long as 15 mins. at this temperature, generally under 8 mins., the influence on the experiments below was

neglected.

Calculation of Collision Efficiency.

The collision efficiency of atomic hydrogen with hydrazine is by definition the ratio of the number of effective collisions to the total number of collisions. In appropriate units this may be expressed by

$$\text{Coll. Eff.} = \frac{d[N_2H_4]/dt}{[H][N_2H_4](\sigma_H + \sigma_{N_2H_4})^2 \left\{ 8\pi RT \left(\frac{1}{M_H} + \frac{1}{M_{N_2H_4}} \right) \right\}^{\frac{1}{2}} \cdot V}$$

where σ_H is the radius of atomic hydrogen and $\sigma_{N_2H_4}$ that of hydrazine, M_H and $M_{N_2H_4}$ are the molecular weights of atomic hydrogen and hydrazine respectively, and V is the volume of the reaction system.

The term $d[N_2H_4]/dt$ has been calculated from the increase in non-condensable gas pressure during the course of the reaction, assuming a reaction mechanism

$$H + N_2H_4 \rightarrow NH_3 + \tfrac{1}{2}N_2 + H_2$$

Corrections have been made for the loss of pressure by withdrawal of doses and for the decrease due to hydrogen being used up in reducing hydrazine. Table (4) gives the values of this term at different temperatures. Owing to the very strong absorption of hydrazine by the surface of the reaction system, this method is the only reliable way of measuring the amount of hydrazine decomposed.

The term $[N_2H_4]$ was obtained from direct manometric measurements of the pressure of N_2H_4 introduced.

Table 4.

Run	Temp. °C.	Press. N_2H_4 m.m.	Press. p-H_2 m.m.	Expos. Time mins.	Press. n.c. gas m.m.	Δp n.c. m.m.	$\frac{d[N_2H_4]}{dt}$ m.m./min.	$\frac{d\,N_2+H_2}{dt}$ m.m./min.
3	208	8.8	53.6	0.0	53.6	-	-	-
				2.0	55.2	2.4	1.20	
				4.0	54.8	3.6	0.90	
				6.0	54.6	5.0	0.83	
						(0.8)	0.98=Av.	1.31
4	203	8.5	53.3	0.0	53.3	-	-	
				2.0	54.2	1.9	0.95	
				4.0	53.8	3.5	0.88	
				6.0	54.3	6.0	1.00	
						(1.0)	0.94=Av.	1.24
5	199	8.5	53.3	0.0	53.3	-	-	
				2.0	54.4	2.1	1.05	
				4.0	54.9	4.6	1.15	
				6.0	55.2	6.9	1.15	
						(1.0)	1.12=Av.	1.47
6	209	8.6	54.1	0.0	54.1	-	-	
				2.0	55.5	2.4	1.20	
				4.0	56.2	5.1	1.27	
				6.0	56.6	7.5	1.25	
						(1.0)	1.24=Av.	1.65
16	90	5.2	50.1	0.0	50.1	-	-	
				2.0	50.9	1.7	0.85	
				4.0	50.7	3.3	0.83	
				6.0	50.2	4.6	0.78	
						(0.9)	0.82=Av.	1.09
17	92	5.2	52.1	0.0	52.1	-	-	
				2.0	52.9	1.7	0.85	
				4.0	52.4	3.0	0.75	
				7.0	52.9	5.3	0.76	
						(0.9)	0.79=Av.	1.05
18	93	5.3	52.7	0.0	52.7	-	-	
				2.0	53.0	1.2	0.60	
				4.0	-	-	-	
				6.0	51.3	3.1	0.50	
				8.0	50.3	4.8	0.60	
						(0.9)	0.57=Av.	0.76
19	91	5.3	53.7	0.0	53.7	-	-	
				2.0	54.2	1.4	0.70	
				4.0	53.6	2.0	0.50	
				6.0	53.2	4.0	0.67	
						(0.9)	0.62=Av.	0.83
11	23	4.0	53.1	0.0	53.1	-	-	
				2.0	53.6	1.2	0.60	
				4.0	53.7	2.2	0.55	
				7.0	53.5	3.9	0.56	
						(0.7)	0.57=Av.	0.76
12	22	1.9	53.9	0.0	53.9	-	-	
				2.0	54.5	1.3	0.65	
				4.0	54.1	2.3	0.57	
				6.0	51.9	2.2	0.37	
						(0.7)	0.53=Av.	0.81
13	23	4.6	53.3	0.0	53.3	-	-	
				2.0	54.1	1.5	0.75	
				4.0	53.8	2.6	0.65	
				6.0	54.0	4.2	0.70	
						(0.7)	0.70=Av.	0.93
14	23	4.2	53.4	0.0	53.4	-	-	
				2.0	54.3	1.6	0.80	
				4.0	54.1	2.8	0.70	
				6.0	54.1	4.2	0.70	
				8.0	53.7	5.2	0.67	
						(0.7)	0.72=Av.	0.96
15	23	5.0	52.4	0.0	52.4	-	-	
				2.0	52.9	1.2	0.60	
				5.0	52.4	2.1	0.42	
				8.0	52.3	3.4	0.43	
				11.0	52.1	4.6	0.42	
				14.0	51.9	5.4	0.36	
						(0.7)	0.45=Av.	0.60

Notes on Table 4.

1. The bracketed figures in the Δ p n.c. column are the (independently measured) corrections applied for loss of pressure through withdrawing doses.

2. In all runs only one dose was removed initially. After exposure, however, two doses were sometimes (e.g. Run 3) removed, one for pressure measurement and one for analysis. In the other runs one dose sufficed for both purposes.

3. $d(N_2 + H_2)/dt$ is obtained by multiplying $d[N_2H_4]/dt$ by 4/3.

In calculating the value of the term H from the para hydrogen conversion data, a knowledge of the kinetics of the para-hydrogen conversion is necessary. Geib and Harteck[5] have shown that when para hydrogen is converted by the action of atomic hydrogen, the rate of the conversion is given by

$$u_t = u_o e^{-kt}$$

where u_t and u_o are the percentage para hydrogen contents above the equilibrium value of 25% at time t and $t = 0$ respectively. The value of k is independent of the initial concentration and proportional to the atomic hydrogen concentration employed which confirms a reaction mechanism

$$H + p\text{-}H_2 \rightleftharpoons o\text{-}H_2 + H$$

The rate of conversion is given by

$$\frac{-d[p\text{-}H_2]}{dt} = k_1[p\text{-}H_2][H] - k_2[o\text{-}H_2][H]$$

Now at equilibrium, when $\frac{d[p\text{-}H_2]}{dt} = 0$, since $[o\text{-}H_2] = 100 - [p\text{-}H_2]$

$$\frac{[p\text{-}H_2]}{100 - [p\text{-}H_2]} = \frac{1}{3} = \frac{25}{75}$$

and thus $k_1 = 3k_2$.

Writing p for $[p\text{-}H_2]$, the rate of conversion is thus

$$\frac{-dp}{dt} = 3k_2[H](p-25) - k_2[H](100-p-75)$$
$$= 4k_2[H](p-25).$$

Integration between the limits $p = p_t$ at time t and $p = p_o$ at $t = 0$ gives

$$(p - 25) = (p - 25)\, e^{-4k_2[H]t}$$

or $$u_t = u_o e^{-4k_2[H]t}$$

The velocity constant of the conversion is therefore

$$k = -4k_2[H]$$

This constant is dependent on the atomic hydrogen concentration and it is usual to eliminate this dependency by defining a new constant

$$k^* = \frac{k}{[H]}$$

Numerically this constant is equal to the sum of the velocity constants of the partial reactions, ortho-para and para-ortho conversions, since

$$k = 4k_2 = k_1 + k_2 .$$

The value of k^* has been determined at high temperatures by Farkas[29] and at low temperature by Geib and Harteck in a flow system, using electrically produced hydrogen atoms. Using these values for k^* it is possible to compute stationary hydrogen atom concentrations from the reaction velocity relation

$$u_t = u_o e^{-k^*[H]t}$$

or $$[H] = \frac{\log_e u_o / u_t}{k^* t}$$

Experimentally it is convenient to determine the time ($t_{\frac{1}{2}}$) required to convert half of the para hydrogen (in excess of equilibrium) by the given stationary hydrogen atom concentration, since then

$$[H] = \frac{\log_e 2}{k^* t_{\frac{1}{2}}} \quad \ldots\ldots\ldots\ldots (1)$$

When the rate of conversion is small, as it was in the conversions below, it is sufficiently accurate to treat the conversion as a unimolecular reaction and express the velocity of conversion by

$$-\frac{du}{dt} = k\,u$$

where u is, as before, the percentage para hydrogen content in excess of equilibrium.

Integration between the limits $u = u_t$ when the time is t and $u = u_o$ when $t = 0$ gives

$$-kt = \log u$$

$$\text{or} \quad t_{\frac{1}{2}} = \frac{\log_e 2}{k^*}$$

$$= \frac{\log_e 2.u}{du/dt}$$

Substituting this value for $t_{\frac{1}{2}}$ in (1)

$$[H] = \frac{du/dt}{k^* u} \quad \ldots\ldots\ldots\ldots (2)$$

Before the stationary atom concentration can be computed from (2), however, the observed data of du/dt

require to be corrected for two factors (a) the accumulation of nitrogen, and (b) the apparent conversion due to n-H_2 formed in the course of the reaction. The method and theory of correcting for (a) is given in the Apparatus Section (page 24). The correction for (b) is given by the following expression

$$\text{True } \%\ p\text{-}H_2 = \frac{n.p. + 25\,\Delta p}{100\,(p + \Delta p)}$$

where n is the observed % para hydrogen content, p and Δp are the respective pressures of para hydrogen and added normal hydrogen. The values of Δp must incorporate a correction for hydrogen disappearing by reaction with hydrazine. The data for $d(N_2 + H_2)/dt$ in Table 4 incorporates this correction and therefore they required only to be multiplied by 2/3 to obtain the values of Δp. Table 5 gives the data of the runs in Table 4 which are used to compute du/dt.

Table 5.

Run	Temp.	Expos. Time	%p-H_2	Press. H_2	Δp_{n-H_2}	Corr. %p-H_2	log %p-H_2	-du/dt
3.	208	0.0	68.6	53.6	-	68.6	1.836	-
		2.0	68.3	54.3	1.7	69.6	1.843	+ve
		4.0	65.3	54.0	1.7	68.0	1.832	0.15
		6.0	63.9	53.7	1.7	67.8	1.831	0.13
								0.14 (Av.)
4.	203	0.0	68.6	53.3	-	68.6	1.836	-
		2.0	66.3	54.0	1.7	67.7	1.831	0.45
		4.0	64.1	53.7	1.7	66.8	1.825	0.45
		6.0	61.4	53.4	1.7	65.4	1.816	0.53
								0.48 (")
5.	199	0.0	68.6	53.3	-	68.6	1.836	-
		2.0	67.0	54.3	2.0	68.5	1.836	0.05
		4.0	65.1	54.3	2.0	68.1	1.833	0.13
		6.0	62.9	54.3	2.0	67.3	1.828	0.22
								0.13 (")
6.	209	0.0	68.6	54.1	-	68.6	1.836	-
		2.0	66.5	55.3	2.2	68.4	1.835	0.10
		4.0	64.2	55.5	2.2	67.8	1.831	0.20
		6.0	-	-	-	-	-	-
								0.15 (")
16.	90	0.0	68.3	50.1	-	68.3	1.834	
		2.0	66.6	50.6	1.4	68.1	1.833	0.10
		4.0	65.0	50.2	1.4	67.7	1.831	0.15
		6.0	-	-	-	-	-	-
								0.13 (")
17.	92	0.0	68.3	52.1	-	68.3	1.834	-
		2.0	66.6	52.6	1.4	67.8	1.831	0.25
		4.0	65.1	52.2	1.4	67.6	1.830	0.18
		7.0	63.4	52.5	2.1	67.5	1.829	0.11
								0.18 (")
18.	93	0.0	63.3	52.7	-	63.3	1.801	-
		2.0	61.7	52.8	1.0	62.4	1.795	0.45
		4.0	60.8	52.0	1.0	62.2	1.794	0.23
		6.0	60.3	51.2	1.0	62.3	1.795	0.16
		8.0	58.6	49.5	1.0	61.3	1.788	0.25
								0.27 (")
19.	91	0.0	63.3	53.7	-	63.3	1.801	-
		2.0	61.8	53.9	1.1	62.5	1.796	0.40
		4.0	61.0	53.2	1.1	62.3	1.795	0.25
		6.0	57.2	52.5	1.1	60.2	1.780	0.50
								0.38 (")
11.	23	0.0	64.8	53.1	-	64.8	1.812	-
		2.0	63.8	53.4	1.0	64.6	1.810	0.10
		4.0	62.4	53.0	1.0	63.9	1.806	0.23
		7.0	60.5	53.1	1.5	63.0	1.799	0.30
								0.21 (Av.)
12.	22	0.0	68.3	53.9	-	68.3	1.834	-
		2.0	66.8	54.3	1.1	67.7	1.831	0.30
		4.0	65.8	54.0	1.1	66.5	1.823	0.18
		6.0	-	-	-	-	-	-
								0.24 (")
13.	23	0.0	68.3	53.3	-	68.3	1.834	-
		2.0	68.1	53.8	1.2	69.1	1.839	+ve
		4.0	65.9	53.6	1.2	67.8	1.831	0.13
		6.0	63.8	53.4	1.2	66.6	1.824	0.27
								0.20 (")
14.	23	0.0	68.3	53.4	-	68.3	1.834	-
		2.0	66.9	54.0	1.3	68.0	1.833	0.15
		4.0	65.2	53.9	1.3	67.3	1.828	0.25
		6.0	63.8	53.8	1.3	66.9	1.825	0.23
		8.0	63.0	53.7	1.3	67.0	1.826	0.16
								0.19 (")
15.	23	0.0	68.3	52.4	-	68.3	1.834	-
		2.0	65.4	52.5	0.8	66.1	1.820	(1.1)
		5.0	65.2	52.3	1.2	66.8	1.825	0.30
		8.0	64.0	52.1	1.2	66.5	1.823	0.23
		11.0	62.0	51.9	1.2	65.4	1.816	0.26
		14.0	60.4	51.7	1.2	64.7	1.811	0.25
								0.26 (")

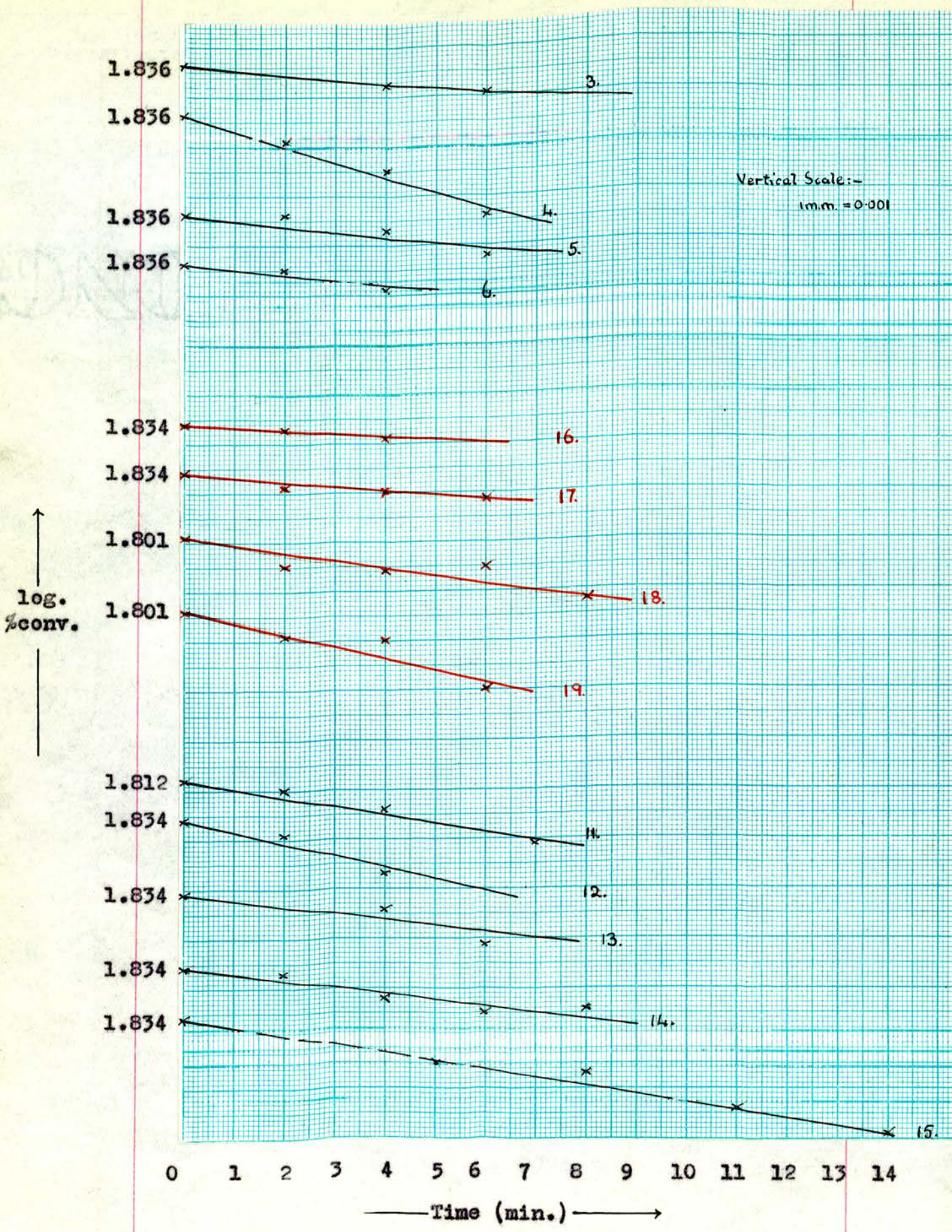


Fig. 2. Graph of log. %conversion against time

Notes on Table 5.

1. In column 4, the change in percentage para hydrogen with time is corrected for nitrogen produced in reaction.

2. The pressure of hydrogen is computed on the basis that the loss of pressure by withdrawing doses is loss of hydrogen only. The error so introduced is negligible.

3. The log % p-H_2 values have been plotted against time in Figure (2) in order to demonstrate the satisfactorily linear relationship.

The collision efficiencies have been calculated from the data in Tables 4 and 5 in the following manner.

$$\text{Coll. Eff.} = \frac{d[N_2H_4]/dt}{[N_2H_4][H] \times (\sigma_H + \sigma_{N_2H_4})^2 \{8\pi RT(\frac{1}{M_H} + \frac{1}{M_{N_2H_4}})\}^{\frac{1}{2}} \times V}$$

$$= \frac{d[N_2H_4]/dt \; k^* u}{du/dt \; [N_2H_4](\sigma_H + \sigma_{N_2H_4})^2 \{8\pi RT(\frac{1}{M_H} + \frac{1}{M_{N_2H_4}})\}^{\frac{1}{2}} \times V}$$

And substituting the data for Run 3

$$= \frac{0.98 \times 43.6 \times 6.76.10^{7} \times 60}{8.8 \times 0.14 \times 1.70.10^{-9} \times 6.06\ 10^{20} \times 60 \times 110}$$

$$= 4.38.10^{-5}$$

In Table 6 are tabulated the other results. The values of $[H]$ have been abstracted for reference.

Table 6.

Collision Efficiencies.

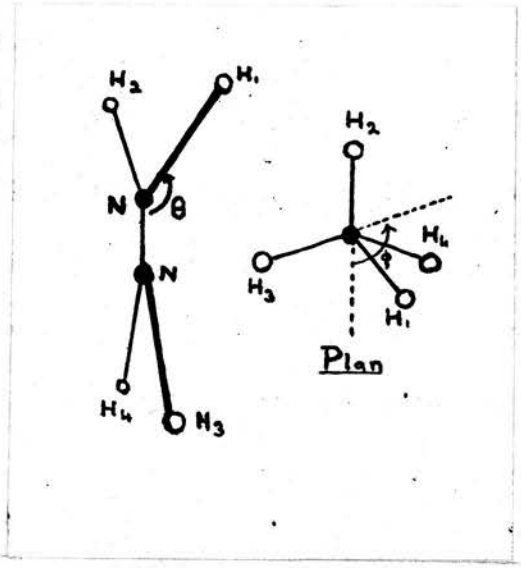
Run	Temp. °C.	$10^3/T$	k* F.	k* G. & H.	[H] moles/litre k^*_G	[H] moles/litre k^*_{G+H}	Coll Eff. k^*_G	Coll Eff. k^*_{G+H}	Mean C.E. k^*_G	Mean C.E. k^*_{G+H}
	208	2.08	$6.76\ 10^7$	$2.88\ 10^7$	$8.03\ 10^{-13}$	$1.88\ 10^{-12}$	$4.38\ 10^{-5}$	$1.87\ 10^{-5}$		
	203	2.10	$6.46\ 10^7$	$2.69\ 10^7$	$2.84\ 10^{-12}$	$6.82\ 10^{-11}$	$1.54\ 10^{-5}$	$6.41\ 10^{-6}$		
	199	2.12	$6.03\ 10^7$	$2.51\ 10^7$	$8.24\ 10^{-13}$	$1.98\ 10^{-12}$	$4.96\ 10^{-5}$	$2.07\ 10^{-5}$		
	209	2.08	$6.76\ 10^7$	$2.88\ 10^7$	$8.54\ 10^{-13}$	$2.60\ 10^{-12}$	$5.33\ 10^{-5}$	$2.27\ 10^{-5}$	$4.05\ 10^{-5}$	$1.71\ 10^{-5}$
	90	2.76	$7.94\ 10^6$	$1.99\ 10^6$	$6.30\ 10^{-12}$	$2.52\ 10^{-11}$	$5.21\ 10^{-6}$	$1.31\ 10^{-6}$		
	92	2.74	$8.32\ 10^6$	$2.19\ 10^6$	$8.33\ 10^{-12}$	$3.17\ 10^{-11}$	$4.12\ 10^{-6}$	$1.57\ 10^{-6}$		
	93	2.73	$8.71\ 10^6$	$2.29\ 10^6$	$1.35\ 10^{-11}$	$5.14\ 10^{-11}$	$1.65\ 10^{-6}$	$4.34\ 10^{-6}$		
	91	2.75	$8.13\ 10^6$	$2.09\ 10^6$	$2.03\ 10^{-11}$	$7.90\ 10^{-11}$	$1.11\ 10^{-6}$	$3.39\ 10^{-7}$	$3.02\ 10^{-6}$	$9.38\ 10^{-7}$
	23	3.38	$1.10\ 10^6$	$1.70\ 10^5$	$7.99\ 10^{-11}$	$5.17\ 10^{-10}$	$3.84\ 10^{-7}$	$5.93\ 10^{-8}$		
	22	3.39	$1.07\ 10^6$	$1.62\ 10^5$	$8.63\ 10^{-11}$	$5.70\ 10^{-10}$	$8.00\ 10^{-7}$	$1.21\ 10^{-7}$		
	23	3.38	$1.10\ 10^6$	$1.70\ 10^5$	$7.19\ 10^{-11}$	$4.59\ 10^{-10}$	$4.45\ 10^{-7}$	$6.88\ 10^{-8}$		
	23	3.38	$1.10\ 10^6$	$1.70\ 10^5$	$6.65\ 10^{-11}$	$4.30\ 10^{-10}$	$4.94\ 10^{-7}$	$7.63\ 10^{-8}$		
	23	3.38	$1.10\ 10^6$	$1.70\ 10^5$	$9.11\ 10^{-11}$	$5.90\ 10^{-10}$	$2.13\ 10^{-7}$	$3.29\ 10^{-8}$	$4.67\ 10^{-7}$	$7.17\ 10^{-8}$

Notes on Table 6.

1. In the missing runs 1, 2, 7, 8, 9, 10, the mercury arc intensity was too low, the conversions being within experimental error.

2. Vol. of Reaction Vessel = 110 c.c.

3. The data used in evaluating the radius and mass factor in the denominator are given below. The values at 200°C., 90° C. and 23°C. were $1.70\ 10^{-9}$, $1.20\ 10^{-9}$ and $1.16\ 10^{-9}$, respectively.



Structure of Hydrazine
(Penney and Sutherland)

In calculating these collision efficiencies, two quantities had to be computed from data in the literature, (a) the radius of hydrazine, (b) the values of k^*. No experimental values are available for (a), but Penney and Sutherland[30] have made a theoretical study of the hydrazine molecule. They consider it is analogous to the hydrogen peroxide molecule in many respects and ascribe to it a structure as depicted. They believe this to be a more stable configuration than $\phi = 180^\circ$ on the grounds that, though simpler, the latter would not possess a magnetic moment which hydrazine has been shown to have by experiment. Taking N-N bond as 1.5 °A and N-H as 1.02 °A, the value of ϕ is 100° from wave function calculations, if θ is assumed to be 110° in analogy to hydrogen peroxide. For the present purposes, however, it is sufficient to take a large value for the radius of the sphere of influence of hydrazine. As an approximation this radius has been taken as the distance from the mid-point of the N-N link to the extension of the N-H link by the sphere of influence of

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1. Estimated from Badger's formula for oscillation of such a bond as H_2N-NH_2 (J. Chem. Phys., 2 : 218, 1934).
2. Infra red data (Dennison & Uhlenbeck, Phys. Rev., 41 : 313, 1932).

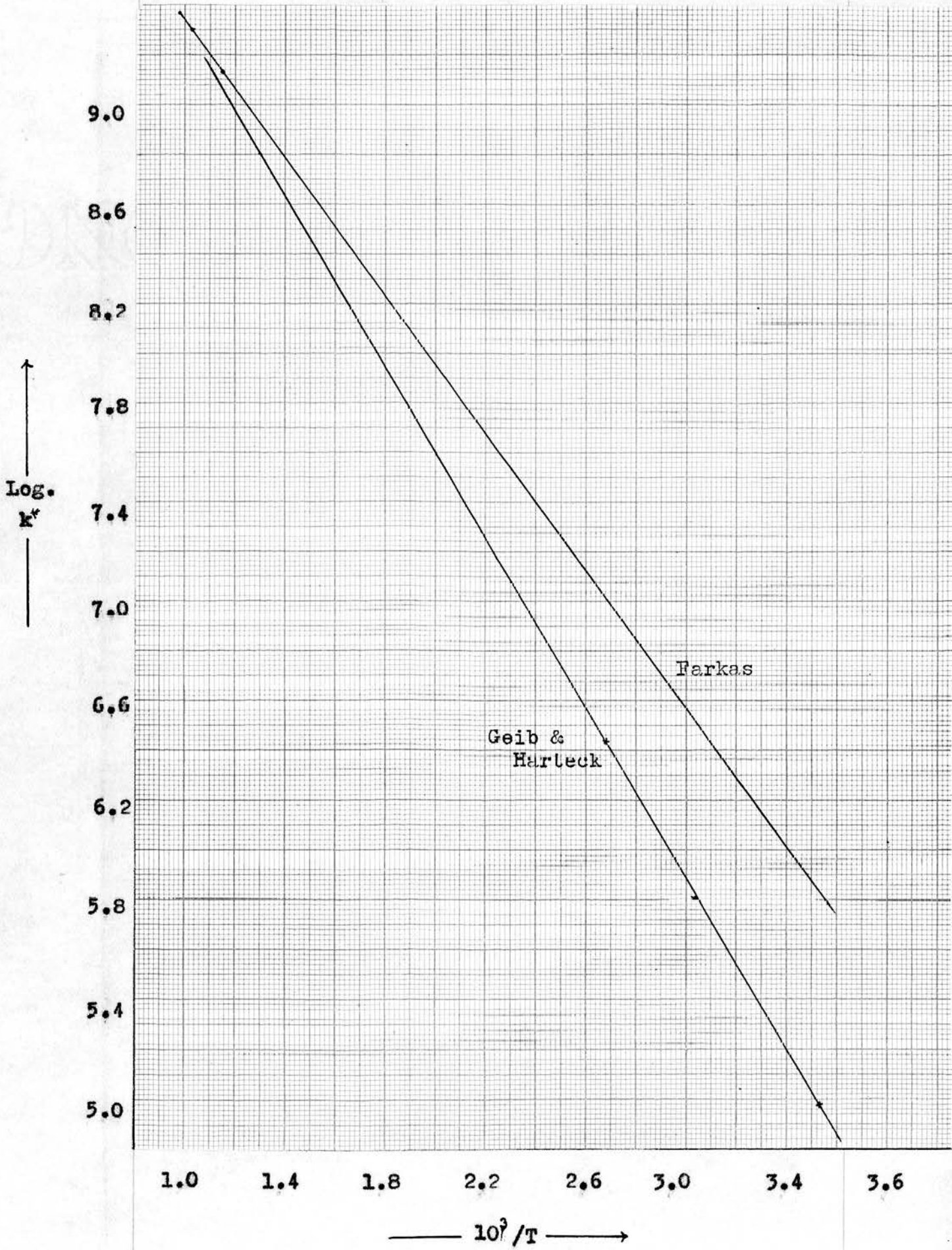


Fig. 3. Extrapolation of values of k^*.

hydrazine. As an approximation this radius has been taken as the distance from the mid-point of the N-N link to the extension of the N-H link by the sphere of influence of the H-atom to which has been ascribed a value 0.27° A. The computed radius is $2.65.10^{-8}$ cms.

For k^{*} have been taken the values of A. Farkas and Geib & Harteck. The former author made his determinations at high temperature ($600-1000^{\circ}$ C.) by thermal conversion experiments and the latter obtained their values at low temperature ($10-100^{\circ}$ C.) from conversions induced by hydrogen atoms produced in a Wood's tube. Unfortunately the values of Farkas when extrapolated to low temperatures differ from those of Geib & Harteck by a factor of ten (shown in Table (7) and graphically in Fig. 3 . Considering the extent of the extrapolation, the discrepancy is not unexpected. In preference to taking the mean value, to which no significance could be attached, the collision efficiencies have been computed for both values. These values may be taken as limiting collision efficiencies until the kinetics of the para hydrogen conversion are finally settled.

Table 7.

Values of k^* Computed from Geib & Harteck's Data.

Temp.	$10^3/T$	Computed k^*	log k^*
°C.		moles^{-1} litre sec^{-1}	
10	3.53	$9.48\ 10^4$	4.977
57	3.03	$6.49\ 10^5$	5.812
100	2.68	$2.78\ 10^6$	6.444
Values of k^* by Farkas (Light and Heavy Hydrogen, p.64)			
600	1.15	$1.37\ 10^9$	9.137
650	1.08	$1.22\ 10^9$	
700	1.03	$2.00\ 10^9$	9.301
750	0.98	$2.38\ 10^9$	9.377

As has already been mentioned, para hydrogen conversion can proceed by two mechanisms, namely by (a) dissociation, and (b) exchange. It will be shown later (page 97) that even at room temperature exchange is fifteen times more efficient than dissociation. However in presence of hydrazine, the rate of para conversion is cut down by a factor of twenty and hence it might be supposed that an error would be introduced in calculating the stationary hydrogen atom concentration. That such an error is practically negligible is shown by the following consideration. The equation expressing H is

$$\frac{d[H]}{dt} = f(I) - k\,[H][N_2H_4] - k_a[H] - k_b[H]^2 = 0$$

In absence of hydrazine the third and fourth terms are of a comparable order of magnitude.[27] In presence of

hydrazine the value of $[H]$ is reduced so much that the fourth term becomes negligible in comparison with the third. Hence

$$[H] = \frac{f(I)}{k_1[N_2H_4] + k_2}$$

Assuming for the sake of argument that pure para hydrogen is being converted, then

$$-\frac{d[p\text{-}H_2]}{dt} = k[H][p\text{-}H_2] + k_2H$$

The two terms represent conversion by exchange and by combination at the wall respectively. And from the equation it will be seen that the relative probabilities of the mechanism for conversion are unaffected by the presence of hydrazine and therefore the correction can be neglected in the present circumstances. At 100° C. and at 200°C., the exchange conversion is so much higher (at 200° C. 1500 : 1) that the correction is completely negligible.

Activation Energy.

The activation energy of the reaction of atomic hydrogen with hydrazine has been completed by plotting the logarithm of the collision efficiency against the reciprocal of the temperature (Fig.4). The basis of this method can be seen from the following:-

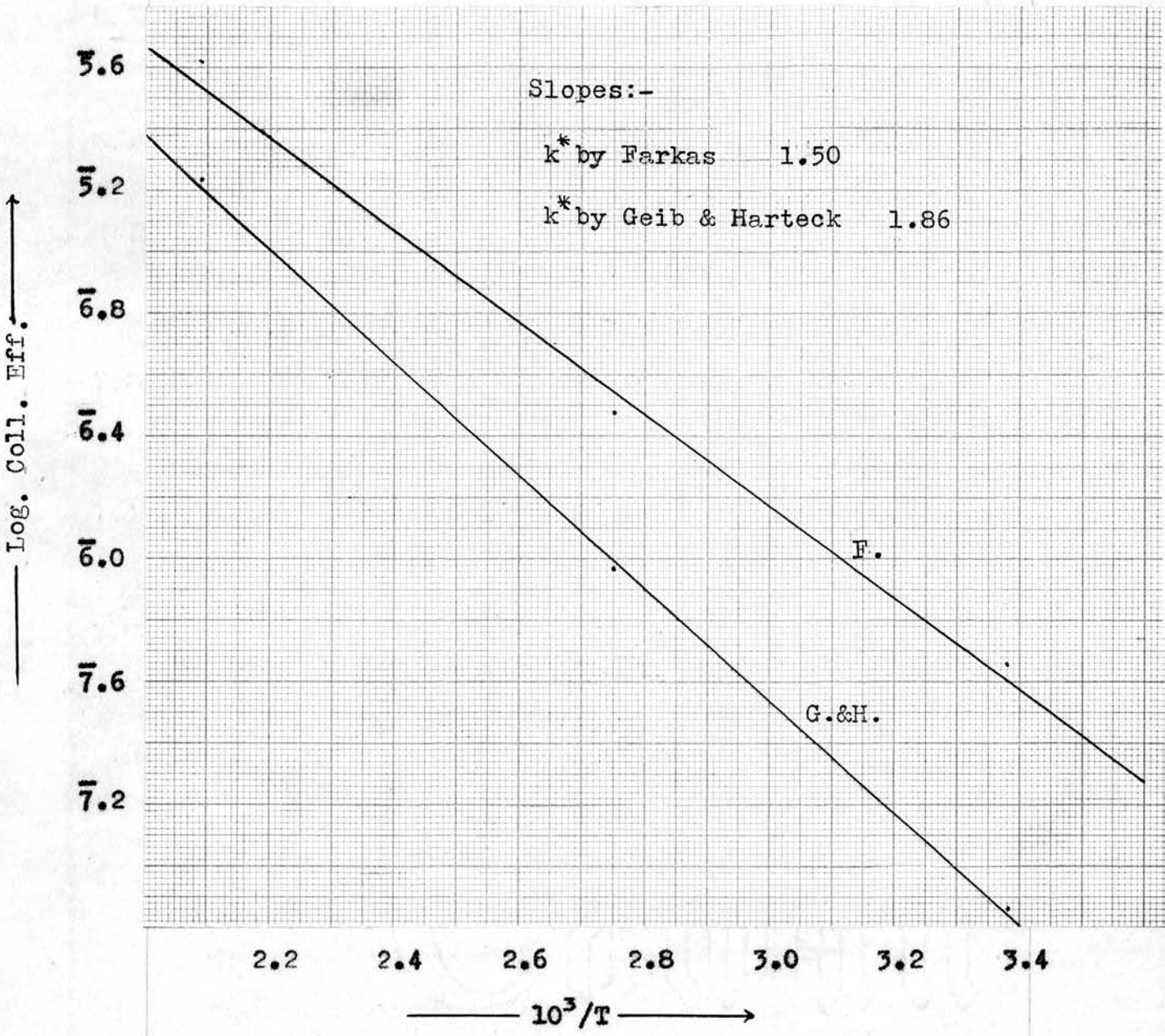


Fig. 4. Graph of log. collision efficiency against $10^3/T$.

$$\mathcal{E} = 6e^{-E/RT}$$

where $\mathcal{E}$ is collision efficiency, 6 is the steric factor (substantially constant over a temperature range) and E is the activation energy. Thus

$$E = 4.57 \frac{\log_{10}\mathcal{E}}{1/T}$$

The values of E obtained from the slopes of graphs in Fig. 4. are given in Table 8.

Table 8.

k^*	Activation Energy cals.
Farkas [29]	6850
Geib & Harteck [5]	8640

Since the energy of activation of the reaction of atomic hydrogen with hydrazine is 6850 cals. or practically the same value as obtained in the exchange reaction

$$H + p\text{-}H_2 \rightleftharpoons o\text{-}H_2 + H$$

it is to be expected that the relative ratio of these two reactions will be temperature independent. The data given on pages 60-62 show that the expectation is realised.

In dealing with the reaction of atomic hydrogen with hydrazine, there is, of course, a possibility of an exchange reaction occurring. For simplicity, an

an exchange reaction involving a polyatomic hydride may be represented in general by

$$D + HX \quad DX + H$$

where X may be NH_2. The nature of X need not be considered during the exchange process except in so far as X may alter the interaction energy of H with the molecule. Consequently, if two similar hydrides such as ammonia and hydrazine are involved in an exchange reaction, it would be expected that the NH_2 part of the hydrazine would behave in almost exactly the same manner as NH_2 in ammonia. Now the energy of activation for exchange in the case of ammonia is 10,000 cals. and therefore there is good reason to believe a similar value would be obtained for hydrazine. But the energy of activation for decomposition by atomic hydrogen is only 6850 cals. and thus it is extremely unlikely that any true exchange could be detected in this reaction. It is not improbable that this may turn out to be a general phenomenon with polyatomic hydrides which are capable of being reduced, sometimes accompanied by disruption by the atomic hydrogen.

Steric Factor.

The steric factor of the reaction of atomic hydro-

gen with hydrazine has been calculated from the exponential relation between collision efficiency and steric factor on page 70. The values obtained are tabulated in Table 9.

Table 9.

Temp.	Steric Factor	
	E = 6.85 K.cals	E = 8.64 K.cals
23°C	$5.33\ 10^{-2}$	$1.76.10^{-1}$
91°C	$3.98\ 10^{-2}$	$1.45.10^{-1}$
205°C	$5.51\ 10^{-2}$	$1.38.10^{-1}$

The only bimolecular reactions of atomic hydrogen in which the steric factors have been calculated are exchange processes with p-H_2 (0.07), NH_3 (0.1), PH_3 (0.3), CH_4 (0.2). It will be noted that all the values lie between 0.1 and unity, i.e. the reactions are normal. The steric factor for hydrazine (10^{-1} to 10^{-2}) is somewhat less. Now steric factors are usually attributed to the fact that the interacting molecule must be orientated in a closely specified direction. Thus it would appear in this case that the hydrogen atom may only approach and react with the hydrazine molecule within, on the average, a small solid angle. It must be added, of course, that several directions of approach may possess the same energy of activation.

Quantum Efficiency of Mercury Sensitised Decomposition of Hydrazine.

The mercury sensitised decomposition of hydrazine has been investigated by Elgin and Taylor.[17] By comparing this reaction with that of hydrogen and oxygen in the same system they arrive at a quantum efficiency twice that of the latter reaction, and they conclude that the quantum efficiency must be at least 13.

The authors consider that this high efficiency is due to a chain reaction.

(1) $N_2H_4 + Hg = N_2H_3 + H + Hg$

(2) $N_2H_3 + N_2H_4 = 2NH_3 + N_2 + H$

(3) $H + N_2H_4 = N_2H_3 + H_2$

It has already been shown that the fraction of excited mercury molecules deactivated by hydrazine molecules in a mixture of 10 m.m. hydrazine and 50 m.m. hydrogen is small. But if such a chain reaction involving hydrogen atoms did occur, this fraction could not be neglected in the para hydrogen conversion method of determining the collision efficiency of atomic hydrogen with hydrazine. Reaction (3) has been shown by the determination of the quantum efficiency of the reaction of atomic hydrogen with hydrazine (page 30) to be a simple re-

action not involving a chain mechanism. In view of this fact the quantum efficiency has been determined again in the present work, this time against the uranyl actinometer.

The reaction system and the technique employed in measuring the 2537 Å quanta by the uranyl oxalate actinometer was exactly the same as in the determination of the quantum efficiency of the reaction of hydrogen atoms with hydrazine. The decomposition of the hydrazine was measured by observing on a Pirani gauge the pressure of non-condensable gas produced. The composition of the non-condensable gas was determined by a separate series of experiments. Typical analyses carried out with the micropirani gauge, are given in Table 1.

Table 1.

Composition of Non-Condensable Gas.

Press. N_2H_4 m.m.	% Decomposition	Temp. °C.	% N_2
5.6	11.9	19.6	49.1
6.2	24.2	20.5	50.8
4.6	24.7	16.1	51.2
5.6	33.3	20.2	51.2

It will be seen that the ratio of hydrogen to nitrogen is close to unity and accordingly the number of

molecules of hydrazine decomposed has been computed from the stoichinometric equation of Elgin & Taylor

$$2\ N_2H_4 = 2\ NH_3 + N_2 + H_2$$

The Pirani gauge, which was protected from hydrazine by cooling the U-tube before it (Apparatus Section, page 18) was calibrated for mixtures of 1 : 1 hydrogen and nitrogen by means of a McLeod Gauge.

Extended decomposition runs showed the same rapid increase of total pressure to twice the initial pressure followed by a much slower increase as observed by Elgin & Taylor. The runs in Tables 1 and 2 were all in the initial fast stage of the reaction. In Table 2 are summarised the quantum efficiency determinations.

Table 2.

Press. N_2H_4 m.m.	$\Delta p_{n.c.}/dt$ m.m./min.	$-d[N_2H_4]/dt$ mols./min.	Relative Intensity mls. $\cdot$01N $KMnO_4$	Total hv hv/min	γ
11.0	0.044	$2.0\ 10^{17}$	0.54	$1.3.10^{18}$	0.39
8.0	0.039	$1.8\ 10^{17}$	0.54	$1.3.10^{18}$	0.34
2.7	0.034	$1.6\ 10^{17}$	0.54	$1.3.10^{18}$	0.30
10.0	0.048	$2.2\ 10^{17}$	0.60	$1.4.10^{18}$	0.39
10.0	0.044	$2.0\ 10^{17}$	0.54	$1.3.10^{18}$	0.39
				Mean	0.36

Temp. 20° C. Reaction Volume = 140 c.c.

2537° A hv = 39% Total hv. 0.54 mls. 0.01 N.$KMnO_4$ $\equiv 1.3\ 10^{18}$ hv/min

The value of 0.36 obtained for the quantum efficiency by this direct determination establishes that this reaction does not proceed by a chain mechanism as suggested by Elgin & Taylor. The two most probable primary dissociations are (1) disruption at the N-N link or (2) disruption of the N-H link

$$(1)\quad N_2H_4 + Hg^* \rightarrow NH_2 + NH_2 + Hg$$

$$(2)\quad N_2H_4 + Hg^* \rightarrow N_2H_3 + H + Hg$$

Since Elgin & Taylor have shown that ammonia is formed as a product of decomposition (1) is contradiction of a quantum efficiency of unity or less. And even if the amine radicals reacted with hydrazine to form ammonia it would require to be a triple collision process

$$2\ NH_2 + N_2H_4 \rightarrow 2\ NH_3 + H_2 + N_2$$

Further, it is very improbable that the amine radicals could interact in any other way than to form nitrogen and hydrogen or to regenerate hydrazine. On the whole (2) is to be preferred, since the formation of ammonia can be explained by the interaction of the N_2H_3 radicals and by the atomic hydrogen attacking hydrazine. The latter process, of course, would imply a quantum efficiency greater than unity but it is to be noted

that the quantum efficiency of the process itself was found to be 0.2 (per H-atom). Since an overall quantum efficiency of at least two is to be expected, the low efficiency observed can be due only to inefficiency of the primary process. This inefficiency may be due either to hydrazine deactivating excited mercury atoms without necessarily dissociating or to an efficient reversal of the primary process. But the latter would require to be more than usually efficient since the probability of collisions between the primary products is extremely small compared with collisions with further molecules of hydrazine which, in the case of atomic hydrogen at least, are reactive. Until there is definite evidence of a back reaction, it seems preferable to adopt the former explanation that the primary process, whatever it be, is not 100% efficient and to bear in mind the observed inefficiency of the reaction of atomic hydrogen with hydrazine.

At the moment there is no known technique of distinguishing the two possible primary modes of reaction. The method adopted by Bolland and Melville[37] in the case of exchange between deuterium and phosphine of determining the fraction of exchange with atomic deuterium

due to a reversal of

$$PH_3 + Hg^* \rightarrow PH_2 + H + Hg$$

is not applicable here as a means of detecting the primary mode. This is due to the fact that atomic hydrogen requires less energy of activation to decompose hydrazine than to exchange with it.

Effect of Photodecomposing Ammonia on the Mercury Sensitised Conversion of Para Hydrogen.

From the measurements by Farkas and Harteck of the life of hydrogen atoms in the photolysis of ammonia at room temperature, it has been concluded that the atoms are removed from the homogeneous phase by some process in addition to third body recombination and wall recombination. The evidence on which this conclusion is based can be recapitulated here with advantage to the subsequent discussion of this section. The life of the hydrogen atoms was measured at 19° C. and 300° C. by the ratio of the concentration of the atoms to their rate of production. Table (1), which is extracted from their paper, gives the variation of life with temperature and ammonia pressures. The same data are expressed graphically in Fig. 1.

Table 1/

Table 1.

Temp. 19° C. Total Pressure 300 m.m.

NH_3 Mole/litre	Absorbed Quanta sec^{-1} cm^{-3}	[H] Mole/litre	Life of H-atoms (sec)
$8.8\ 10^{-5}$	$6.5\ 10^{13}$	$0.82\ 10^{-9}$	0.0076
$17.6\ 10^{-5}$	$13.0\ 10^{13}$	$1.29\ 10^{-9}$	0.0060
$29.4\ 10^{-5}$	$21.0\ 10^{13}$	$1.47\ 10^{-9}$	0.0043
$32.4\ 10^{-5}$	$22.0\ 10^{13}$	$1.53\ 10^{-9}$	0.0042
$100.0\ 10^{-5}$	$39.0\ 10^{13}$	$1.38\ 10^{-9}$	0.0021
$230.0\ 10^{-5}$	$42.0\ 10^{13}$	$0.74\ 10^{-9}$	0.0011

0.2 third body collision/sec between H + H + M

Temp. 300° C. Total Pressure 700 m.m.

$1.47\ 10^{-5}$	$1.1\ 10^{13}$	$2.06\ 10^{-9}$	0.115
$3.8\ 10^{-5}$	$2.8\ 10^{13}$	$2.24\ 10^{-9}$	0.07
$8.9\ 10^{-5}$	$6.5\ 10^{13}$	$4.76\ 10^{-9}$	0.046
$1.7\ 10^{-4}$	$13.0\ 10^{13}$	$6.46\ 10^{-9}$	0.03
$2.6\ 10^{-4}$	$19.0\ 10^{13}$	$5.28\ 10^{-9}$	0.016
$3.5\ 10^{-4}$	$24.0\ 10^{13}$	$4.76\ 10^{-9}$	0.012
$7.3\ 10^{-4}$	$34.0\ 10^{13}$	$3.24\ 10^{-9}$	0.0057
$14.7\ 10^{-4}$	$41.0\ 10^{13}$	$2.06\ 10^{-9}$	0.003
$29.4\ 10^{-4}$	$43.0\ 10^{13}$	$1.47\ 10^{-9}$	0.002

1 third body collision/sec between H + H + M

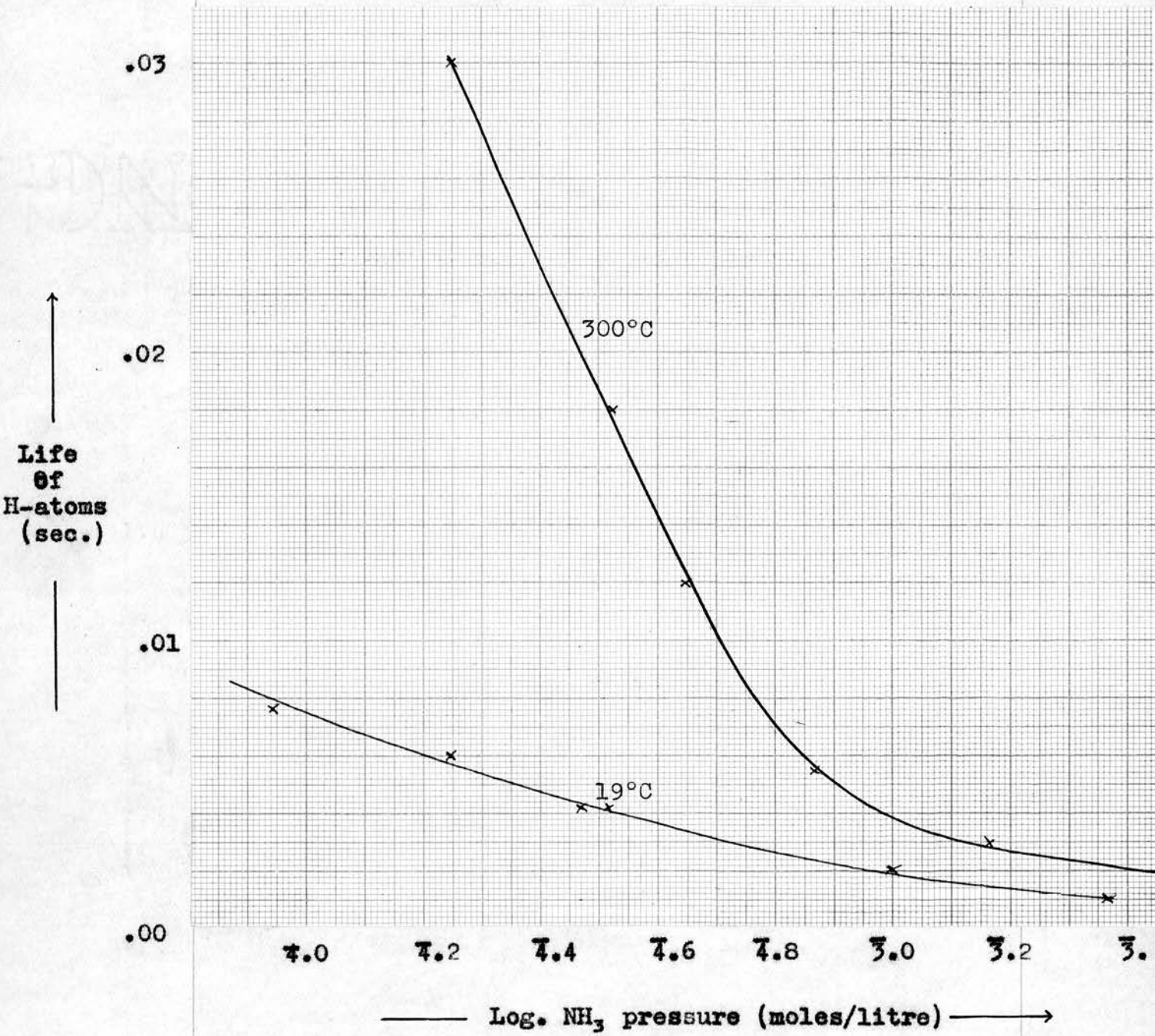


Fig. 1. Comparison of H-atom life at 300°C and 19°C.

It will be observed that the life values have been computed by taking the rate of hydrogen atom production as exactly equivalent to the quanta absorbed by ammonia. An implicit assumption is thus made that the quantum efficiency of the primary process in the photolysis is unity. From Fig. 1 it will be seen that the life of hydrogen atoms at 300° C. relative to that at 19° C. varies with ammonia pressure. Table 2 shows the relative lives at 300° C. and 19° C. at various ammonia pressures.

Table 2.

Press. NH_3 m.m.	Life of H-atom 300°C. sec.	19°C. sec.	Ratio
1.5	0.046	0.0076	6.05
3.4	0.0298	0.0056	5.32
10.0	0.0081	0.0030	2.70
15.0	0.0049	0.0023	2.13
30.0	0.0026	0.0014	1.86

The authors have estimated the rate of removal of hydrogen atoms by third body collisions and diffusion to the walls and conclude that these processes are insufficient to account for the relatively low life of the atoms at 19° C. This is the basis for the con-

clusion that some other process of removal from the homogeneous phase must exist at low temperatures. They themselves suggest that the mechanism of removal is the formation of ammonium radicals

$$NH_3 + H \rightleftharpoons NH_4$$

This hypothesis can easily be tested in an entirely separate manner. If ammonia does in fact remove hydrogen atoms forming ammonium radicals then ammonia ought to have an inhibitory effect on the mercury sensitised conversion of para hydrogen. As the following data from Farkas and Melville[24] (Table 3) show, ammonia has practically no effect on the stationary atom concentration under conditions where according to the ammonium hypothesis a marked diminution would have been expected. The low concentration is therefore not due to this reaction.

Table 3.

Press. p-H_2 m.m.	Press. NH_3	$t\frac{1}{2}$ sec.	Temp.
95.2	-	2.1	238
83.0	19.0	3.0	238

It is this same abnormality in the hydrogen atom concentration which has been advanced as a reason for introducing into the ammonia photolysis the Mund-van

Tiggelen mechanism, involving hydrazine in secondary reactions.

In the present work an attempt has been made to determine quantitatively the rate at which hydrogen atoms are removed, irrespective of the mechanism of removal. The technique adopted in making this investigation consists essentially of measuring reduction in the rate of hydrogen atom exchange conversion of para hydrogen, brought about by this unknown process in the ammonia photolysis. For this purpose ammonia is decomposed by a zinc spark at the same time as para hydrogen is being converted by excited mercury atoms. The system of reactions is thus

$$NH_3 + h\nu \rightarrow NH_2 + H$$

$$H + x \rightarrow \text{unknown, where x might be } NH_3,\ N_2H_4 \text{ etc.}$$

$$p\text{-}H_2 + Hg^{*} \rightarrow H + H + Hg$$

$$H + p\text{-}H_2 \rightarrow o\text{-}H_2 + H$$

$$H + H + M \rightarrow H_2 + M$$

$$NH_2 + NH_2 \rightarrow N_2 + 2H_2 \quad \text{etc.}$$

The question arises as to what ought to be the relative intensities of the arc and spark. It is obvious that the rate of decomposition of ammonia cannot be made so small as to convert the para hydrogen at a rate much smaller than that due to the excited mercury atoms,

since the amount of product, which presumably removes the hydrogen atoms, would be too small to affect the hydrogen atom concentration appreciably. On the other hand if the rate of decomposition of ammonia is very much larger than the rate of production of excited mercury atoms, the ammonia sensitised conversion of para hydrogen will overshadow the mercury sensitised conversion. And, therefore, the effect of the unknown product on the latter reaction will not be detectable. The best compromise appears to be an approximate equality of the intensities.

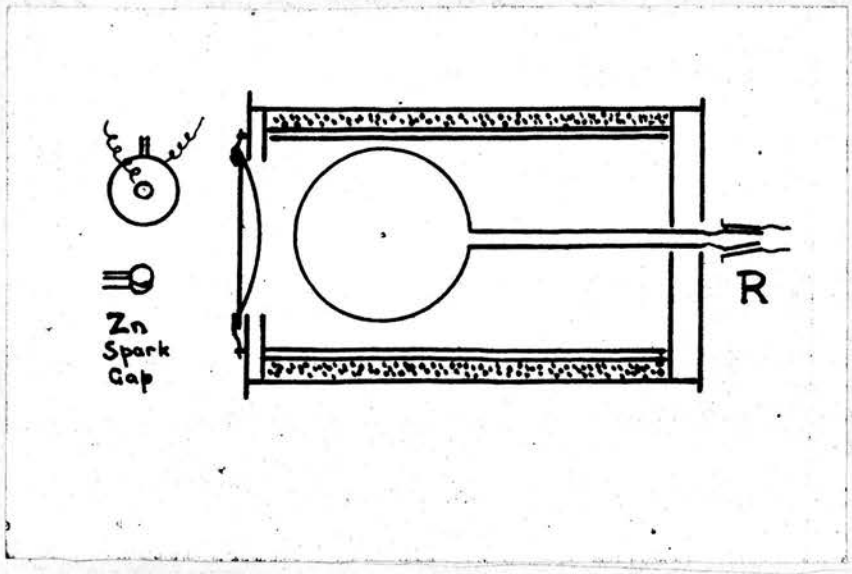
Experimentally, the problem to be solved is the determination of the influence of photodecomposing ammonia on the mercury sensitised conversion of para hydrogen. But there is a difficulty which must be discussed here. Assuming for the moment that the hydrogen atoms are not removed by the products of the ammonia reaction, then the rate of para hydrogen conversion will be given by the following equations

$$\text{Rate (Arc)} = \text{const.}\,(I_a)^x$$

$$\text{Rate (Spark)} = \text{const.}\,(I_s)^x$$

$$\text{Rate (Spark and Arc)} = \text{const.}\,(I_{sa})^x$$

where I is the intensity of the respective sources and x is the intensity exponent. In order to arrive at



Arrangement of Arc Lamp and Spark

the rate of conversion of para hydrogen by the arc in presence of the spark, it is necessary to correct the rate with spark and arc operating together for the contribution made by the spark itself. Thus, the following equations will hold:-

$$\frac{\text{Rate A}}{\text{Rate A}_S} = \frac{\text{const.}(I_a)^x}{\text{Rate (S+A)}}\left(\frac{I_a}{I_s+I_a}\right)^x = \left(\frac{I_s+I_a}{I_s}\right)^x \times \frac{\text{Rate (S)}}{\text{Rate (S+A)}} \quad \ldots (1)$$

If the products of decomposition of ammonia remove hydrogen atoms more effectively than the normal process of combination in the gas phase and on the walls, the magnitude of the above quantity will be greater than unity. Figure (1) shows the arrangement of the reaction system and the sources of radiation. The reaction vessel was a spherical fused silica bulb of about 100 c.c. capacity which could be attached to the pumps, gauges etc. by a ground joint sealed with Picene wax. The electric furnace used to obtain the temperatures desired was the same as in the experiments with atomic hydrogen and hydrazine (page 47). The zinc spark was air cooled by a jet of compressed air. The voltage across the gap was obtained from a transformer with an output of 4 K V.A at 10,000 Volts. The current in the primary circuit was controlled by a

resistance in series. In the experiments the current in the primary circuit was from 17-19 amps at 230 Volts. The source of the 2537° A mercury line was the same mercury vapour lamp used in previous experiments.

The experimental procedure was to introduce 3-30 m.m. of ammonia and 50 m.m. para hydrogen and measure the rate of the mercury sensitised conversion. Fresh para hydrogen was introduced and the rate of conversion by sensitisation by mercury and ammonia together was measured. Finally, the rate of ammonia sensitised conversion was measured with fresh para hydrogen. Approximate measures of the intensities of the arc and spark were made by observing the photolysis of 3-30 m.m. ammonia with the Pirani gauge, assuming quantum efficiencies of 0.1 and 0.25 respectively.

Before the expression (1) on page 85 may be used, it is necessary to evaluate the magnitude of x. This has been done for both spark and arc and a few results are given in Table 4.

$$x = \frac{\log (R/R_i)}{\log (I/I_i)}$$

Source	Conversion Rates	log R	hv/sec.	log hv	x
Spark	.143	2.155	$8.0\ 10^{15}$	15.903	
	.086	1.935	$4.8\ 10^{15}$	15.681	0.81
Arc	.307	2.487	$1.2\ 10^{16}$	16.079	
	.109	2.037	$4.0\ 10^{15}$	15.602	0.98

$d(\log \frac{u_0}{u_1})/dt$

It will be observed that the values lie close enough to unity to justify putting x = 1, which leads to a very great simplification

$$\frac{\text{Rate (A)}}{\text{Rate } (A_s)} = \left(1 + \frac{I_o}{I_s}\right) \times \frac{\text{Rate (S)}}{\text{Rate (S+A)}} = \frac{\text{Rate A + Rate S}}{\text{Rate (S+A)}}$$

The complete results for various temperatures and intensities and at pressures comparable to those employed by Farkas and Harteck are given in Table 5.

Table 5/

Table 5.

emp. °C.	Press. NH_3 m.m.	Press. p-H_2 m.m.	Expos. Time min.	log. (%p-H_2) A	log. (%p-H_2) SA	log. (%p-H_2) S	S + A / SA	Intensity A hv/sec	Intensity S hv/sec
00	50	50	12.0	.276	.320	.082	1.12	$1.2\ 10^{16}$	$4.3\ 10^{15}$
"	50	50	10.0	.792	.700	.193	1.37	$9.4\ 10^{15}$	$4.6\ 10^{15}$
"	50	50	7.0	.477	.589	.063	0.92	$9.4\ 10^{15}$	$3.9\ 10^{15}$
"	30	50	5.5	.281	.356	.074	1.00	-	$2.2\ 10^{16}$
"	30	50	5.5	.553	.528	.089	1.22	-	$2.2\ 10^{16}$
"	30	50	7.0	.449	.526	.100	1.04	$1.5\ 10^{16}$	$8.0\ 10^{15}$
"	30	50	10.0	.399	.496	.086	0.98	$8.0\ 10^{15}$	$4.8\ 10^{15}$
"	30	50	15.0	.163	.297	.107	0.91	$4.0\ 10^{15}$	$9.0\ 10^{15}$
"	30	50	10.0	.307	.397	.091	1.00	$1.2\ 10^{16}$	$4.0\ 10^{15}$
"	5.0	6.5	7.0	.215	.238	.037	1.06	$3.4\ 10^{15}$	$3.4\ 10^{15}$
"	2.0	3.0	12.0	.341	.338	.029	1.10	$2.1\ 10^{15}$	$8.7\ 10^{14}$
50	32	53	20.0	.070	.087	.016	0.99	$7.0\ 10^{14}$	-
"	30	53	15.0	.031	.053	.024	1.04	-	$1.9\ 10^{15}$
"	30	52	14.0	.281	.346	.013	0.85	$3.8\ 10^{15}$	$2.1\ 10^{15}$
"	15	26	12.0	.181	.207	.016	0.95	$3.8\ 10^{15}$	$2.1\ 10^{15}$

It can be seen that in every case the value of the above expression is substantially equal to unity from which it may be concluded that photodecomposing ammonia has no appreciable effect in removing hydrogen atoms at an abnormally fast rate.

Since the conclusion drawn from these experiments is negative, it is desirable to furnish some positive evidence that the conditions were such that a removal of hydrogen atoms was to be expected. For this purpose a repetition of the work of Melville[6] in which the ammonia photolysis was inhibited by atomic hydrogen was most suitable. In Table 6 are tabulated the results of inhibition experiments under the same conditions as employed in the conversion runs.

Table 6.

Temp. °C.	Press. NH_3 m.m.	Press. $p-H_2$ m.m.	Expos. Time min.	Rates of Decomposition A m.m.	SA m.m.	S m.m.	S / SA-A	Intensities A hv/sec	S hv/sec
100	3.0	.090	6	.008	.014	.007	1.17	$2.2 10^{15}$	$8.5 10^{14}$
	3.2	.117	10	.012	.017	.010	2.00		
	3.2	.128	10	.002	.013	.012	1.09		
	3.2	.151	10	.007	.018	.013	1.18		
50	3.5	.152	10	.007	.013	.011	1.83		
	1.8	.178	10	.004	.012	.015	1.88		
	3.6	.175	10	.007	.009	.005	2.50		

It will be observed that inhibition is marked at 50°C.

though less appreciable at 100° C. This is in accordance with expectations since the quantum efficiency increases from 50° C. to 100° C. which, of course, means the back reaction is of decreasing importance at higher temperatures. At the low pressures of these experiments diffusion to the wall of the hydrogen atoms would tend to overshadow any process whereby removal is effected in the gas phase. Consequently, the fact that inhibition which is partly a gas phase phenomenon could be detected, is evidence that conditions at high pressures were such that a removal of hydrogen atoms by a gas phase process could also have been detected.

Life of Hydrogen Atoms.

The life of an atom or a radical is not an absolute physical property, being dependent to such a large extent on the condition of the walls of the reaction vessel, the dimensions of the vessel etc. Since it was intended to make subsequently a measurement of the life of amine radicals (page103) in the same reaction system, the life of hydrogen atoms was determined as a standard of comparison. The choice of hydrogen atoms is dictated simply by the fact that it is most commonly determined.

From theoretical consideration of the para hydrogen conversion by excited mercury atoms, it is found possible to predict the form of the pressure dependence of the absolute rate of conversion. The equation of the rate of conversion is

$$\frac{-d[p\text{-}H_2]}{dt} = k_1[H][p\text{-}H_2] + k_2[H] + k_3[H]^2[x] \quad \ldots (1)$$

where the second term expresses the rate of conversion by diffusion of hydrogen atoms to the walls and the third term the rate of conversion by third body combination of the atoms. At all but very high hydrogen pressures, k_3 is negligible compared with $k_1[p\text{-}H_2]$ and

k_2 and may be set aside for the moment. At intermediate pressures $k_1[p\text{-}H_2]$ is much greater than k_2 and determines the rate of conversion. At low pressures of the order of 1 m.m., the rate is determined by k_2 which overshadows $k_1[p\text{-}H_2]$ in this pressure region. Thus conversion at low pressures is due primarily to dissociation and recombination, the rates of which are controlled by the stationary Hg^* atom concentration and diffusion to the walls, respectively. The stationary excited mercury atom concentration is given by

$$[Hg^*] = \frac{f(I)}{k_4[H_2] + k_5} \quad \ldots\ldots(2)$$

where I is the intensity of the incident radiation, k_4 the velocity constant of deactivation by molecular hydrogen and k_5^{-1} is the mean life of an excited mercury atom. The mean life of the atoms is not constant, being dependent on mercury and hydrogen pressures since imprisonment occurs of the resonance radiation of excited mercury atoms.[44] At low mercury pressures about 10^{-5} m.m. Hg the mean life is $1.07.10^{-7}$ sec. (Garrett, Phys. Rev., 40 : 779, 1932) which increases to 10^{-6} sec. at pressures of 0.001 m.m. Hg corresponding to 15° C. At high hydrogen pressures where a large fraction of the mercury atoms are

deactivated the mean life of the atom will tend towards the lower limit, and at low hydrogen pressures the life will tend to the higher limit. Thus the imprisonment of resonance radiation effect must have a considerable bearing on the conversion of para hydrogen at low pressures. From (1) and (2) the rate of conversion at low pressure is given by

$$-\frac{d[p\text{-}H_2]}{dt} = \frac{f(I)}{1 + \frac{k_5}{k_4[H_2]}} \quad \ldots\ldots\ldots(3)$$

It will be apparent from (3) that for a small pressure range the value of the term $\frac{k_5}{k_4[H_2]}$ will remain substantially constant due to the dependence of k_5 on hydrogen pressure. At the lower limit of this range the value of the term will tend to increase and at the upper limit it will tend to decrease. Thus the pressure dependence curve of the absolute rate of conversion will show either a point or a region of inflexion at low pressures. The duration of this inflexion will be controlled also by the mercury pressure. Since the upper limit of k_5 is set by the mercury pressure, the optimum conditions for detecting the inflexion will require a high mercury pressure.

The pressure dependence of the mercury sensitised

conversion of para hydrogen has been determined in the same reaction system as will be described in detail in Section, p.103 and the results are tabulated in Table 1 . From the curve in Fig.1 it will be seen that the theoretically expected inflexion is well defined. This portion (A-B) of the curve thus represents conversion by dissociation and recombination, while the portion (B-C) represents increasing amount of conversion by exchange of atoms and molecules of hydrogen. Below 1 m.m. of hydrogen the curve shows the expected fall due to the upper limit of k_s being attained. Presumably if the curve had been carried to much higher pressures (200 m.m.), there would have been observed a gradual decrease in the rate of conversion due to the third body collision term k_3 in (1) increasing in importance.

The importance of this easily reproduced inflexion in the pressure dependence curve of the para hydrogen lies in the fact that it provides a ready means of determining the intensity of the 2537° A mercury resonance line. Owing to the imprisonment of resonance radiation effect it is certain that practically every excited mercury atom is deactivated by hydrogen molecules in the region of inflexion. It is also certain

that practically every deactivating hydrogen molecule is dissociated. (On page 40 the suggestion has been made that mercury hydride may sometimes be formed, but this is unstable and would disrupt on a bimolecular collision). Thus the incident intensity of the 2537°A mercury resonance line can be determined in any reaction system simply by measuring the absolute rate of para hydrogen conversion in the inflexion pressure region.

But of even greater importance is the fact that this is an absolute method of determining the rate of production of hydrogen atoms by mercury sensitised dissociation of hydrogen. The rate of production is commonly determined by measuring the incident 2537° A and assuming the former is twice the latter.

Use has been made of this new method of determining hydrogen atom production rate to measure the life of hydrogen atoms in conditions comparable to those which existed in the para hydrogen conversion experiments. The life of hydrogen atoms is conveniently obtained from the ratio

$$\frac{[H]}{d[H]/dt}$$

The rate of production of hydrogen atoms is, of course, twice the number of p-H_2 molecules converted per sec.

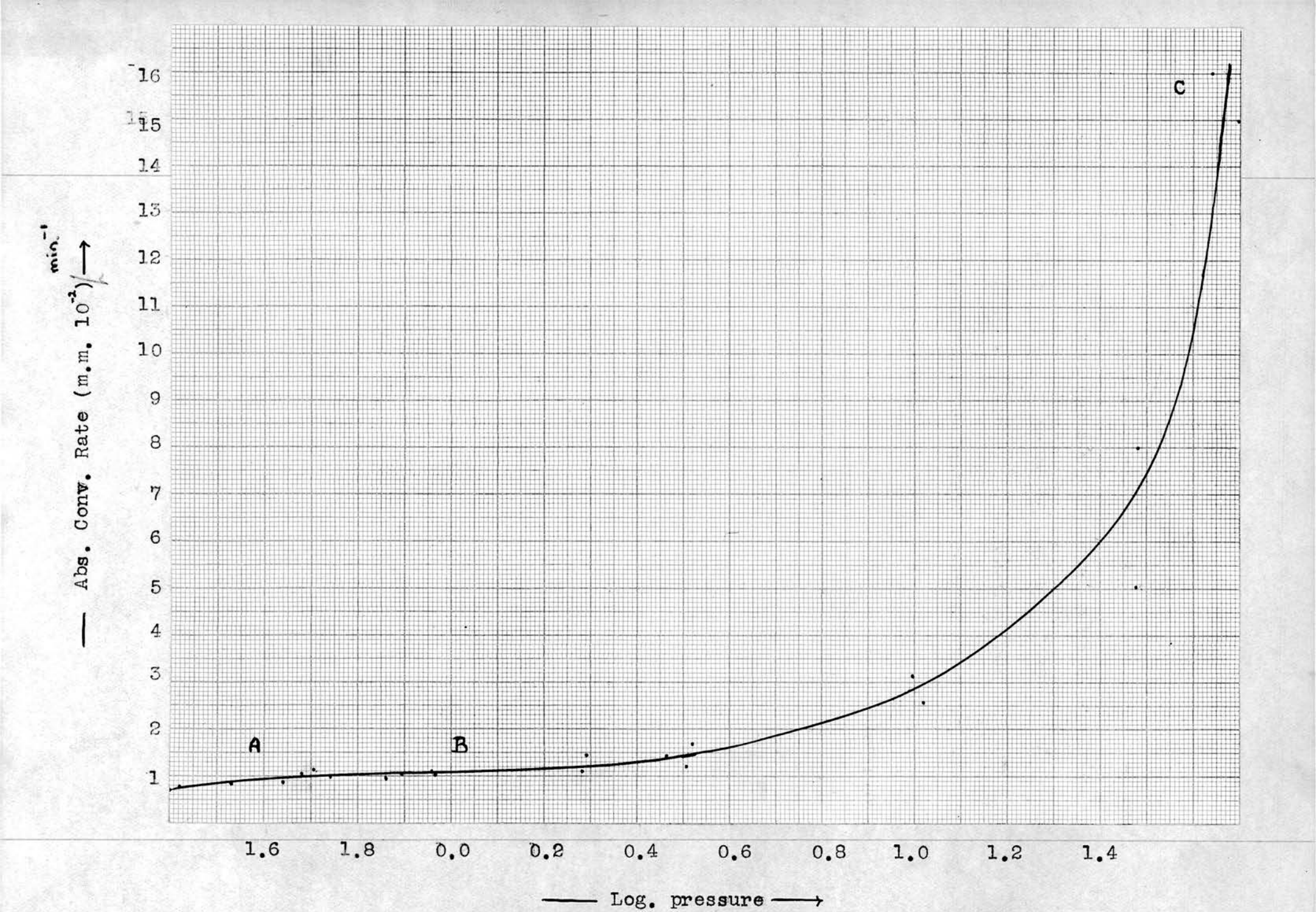


Fig. 1. Pressure dependence of p-H_2 conversion

and the concentration of the atoms is readily obtained in the usual manner (page 60) from the rate of para hydrogen conversion at the pressure in question, which must be such that conversion by exchange occurs.

In Table (1) is given typical data obtained for the pressure dependence of the para-ortho hydrogen conversion.

Table (1)/

Table (1).

Press. $p\text{-}H_2$	log ditto.	Expos. Time.	$-\Delta\%p\text{-}H_2$	Absolute Conversion	Abs. Conv. Rate
0.9	$\bar{1}.959$	5.0	6.1	5.49	1.10
1.9	0.279	10.0	6.0	11.4	1.14
2.9	0.462	15.0	7.5	21.8	1.45
0.51	$\bar{1}.708$	4.0	9.0	4.59	1.15
0.78	$\bar{1}.892$	4.0	5.3	4.13	1.04
0.26	$\bar{1}.415$	5.0	15.2	3.95	0.79
0.34	$\bar{1}.532$	7.0	18.4	6.25	0.89
0.44	$\bar{1}.644$	9.0	17.7	7.78	0.86
0.69	$\bar{1}.839$	12.0	17.7	12.2	1.01
0.92	$\bar{1}.964$	12.0	12.8	11.8	0.98
1.95	0.290	8.0	6.1	11.9	1.49
3.30	0.519	13.0	6.7	22.1	1.70
9.9	0.996	11.0	3.5	34.7	3.15
30.0	1.477	10.0	1.7	51.0	5.10
49.5	1.695	9.0	2.7	134	15.0
0.25	$\bar{1}.398$	6.0	17.2	4.30	0.72
0.48	$\bar{1}.681$	8.0	17.9	8.59	1.07
0.92	$\bar{1}.964$	10.0	11.3	10.4	1.04
3.2	0.508	14.0	5.3	17.0	1.21
10.4	1.017	11.0	2.7	28.1	2.56
30.3	1.481	11.0	2.9	87.9	8.00
44.5	1.648	10.0	3.6	160	16.0
m.m.		min.		m.m. 10^{-2} 100% $p\text{-}H_2$	m.m.10^{-2} 100% $p\text{-}H_2$ min^{-1}

$p\text{-}H_2$ Constant = 56.5%

Volume of Reaction Vessel 97 c.c.

The data in Table (1) is shown graphically in Fig. 1 where the well marked inflexion is apparent. The life of hydrogen atoms has been computed in the following manner.

Rate of Formation of H-atoms.

At the inflexion portion of the pressure dependence

curve the rate of hydrogen atom production is given by

$$\frac{d[H]}{dt} = \frac{200}{u} \frac{d[p\text{-}H_2]}{dt}$$

where u is % para hydrogen content and the 100/u term includes the dissociation of the ortho-hydrogen. Substituting the value of $1.05^{-2}10$ m.m. p-H_2/min. from the graph

$$\frac{d[H]}{dt} = \frac{200}{56.5} \times \frac{1.05\ 10^{-2}}{760} \times \frac{273}{293} \times \frac{97}{22430} \times \frac{1000}{97 \times 60}$$

$$= 3.39\ 10^{-8} \text{ moles/litre/sec}$$

Concentration of H-atoms.

From the graph the rate of para hydrogen conversion at 15 m.m. is $3.7\ 10^{-2}$ m.m. p-H_2/min. and since the rate of conversion by dissociation is $1.05\ 10^{-2}$ m.m./min., the rate of conversion by exchange at 15 m.m. is $2.65\ 10^{-2}$ m.m. p-H_2/min.

Now $[H] = \frac{du/dt}{k^* u}$ (vide page 60)

$$= \frac{2.65\ 10^{-2}}{15 \times 0.565 \times 60 \times k^*} \text{ moles/litre}$$

$$= 5.59\ 10^{-11} \quad k^* = 9.33\ 10^5 \text{ (Farkas)}$$

or $= 3.70\ 10^{-10} \quad k^* = 1.41\ 10^5$ (Geib & Harteck)

Thus Life of H-atom $= \frac{5.59\ 10^{-11}}{3.39\ 10^{-8}} = 1.65\ 10^{-3}$ sec.

or $= \frac{3.70\ 10^{-10}}{3.39\ 10^{-8}} = 1.09\ 10^{-2}$ sec.

The limiting values obtained by this method are of the order of magnitude to be expected from other investigations, e.g. 1 to $8\ 10^{-3}$ sec. over 30 m.m. NH_3 by Farkas and Harteck.

Quantum Efficiency of Primary Process in Ammonia Photolysis.

In view of the facts that hydrazine is not a particularly rapid agent for removal of hydrogen atoms in the ammonia photolysis and that no rapid process of removal has been detected, it was decided to measure the quantum efficiency of the primary process. For the moment it will suffice to say that most of the observations of the behaviour of the ammonia photolysis could be explained by a low quantum efficiency for the primary process. This quantum efficiency has been implicitly assumed as unity by all previous workers. It is evident that appearance of a predissociation spectrum is not necessarily a quantitative demonstration that all molecules undergo primary photodissociation.

In selecting a method to test this assumption, the criterion is that it must not involve any further assumptions. With this in mind, it was elected to determine the rate of production of hydrogen atoms which would convert para hydrogen at the same rate as the photolysis of ammonia by a given intensity of radiation. The ratio of the rate of production of hydrogen atoms to the intensity, in terms of quanta absorbed by

ammonia, is a direct measure of the quantum efficiency of the ammonia primary process. The rate of production of hydrogen atoms by mercury sensitised dissociation of hydrogen can be determined by the "inflexion method" (page 91). This is a direct measurement which involves no assumption of the efficiency of deactivation of mercury atoms and thus is an absolute standard by which the rate of production of hydrogen atoms in the ammonia photolysis can be evaluated.

The reaction vessel was the same as was employed in determining the life of hydrogen atoms and amine radicals. The cylindrical sector, of course, was not used. The experimental procedure was to arrange the mercury discharge lamp and the spark at distances from the reaction vessel such that the rates of p-H_2 conversion by these agents were very nearly the same. The pressure of para hydrogen was about 50 m.m. and about 30 m.m. ammonia was used to sensitise conversion by the spark. A few determinations of the absolute rate of conversion of para hydrogen at pressures within the inflexion region of the pressure dependence curve served to establish the rate of hydrogen atom production by the mercury discharge lamp. The number of quanta absorbed by ammonia in promoting the

same rate of conversion as the mercury sensitised production of hydrogen atoms, was observed by a separate exposure of the ammonia to the spark when the non-condensable gas formed was determined by a Pirani gauge. In order to test the constancy of the spark output, an ammonia photometer (described in the Amine Radical Life Reaction, page103) was placed behind the spark. Any small inconstancy between the ammonia sensitised para-hydrogen conversion exposure and the quanta determination exposure could be corrected by the photometer readings. In calculating the quanta absorbed by the ammonia the overall quantum efficiency was taken to be 0.24 from Wiig's measurements of the pressure dependence.

In Table (1) are arranged the results of all the determinations. When the rates of conversion by photo-produced atomic hydrogen and by ammonia sensitisation were not exactly the same, the spark intensity which would require to be absorbed by the ammonia to bring about the same rate of conversion, was computed from the intensity exponent of the ammonia sensitised con-version. The value which was taken for the exponent was that determined earlier (vide page 86) of 0.81.

The quantum efficiency of the primary process in the ammonia photolysis is thus given by

$$= \frac{d[H_{NH_3}^*]/dt}{(h\nu/sec)_x \sqrt{(R_H/R_{NH_3})}}$$

where $[H_{NH_3}]/dt$ is the rate of production of atomic hydrogen by mercury sensitisation, hv/sec is the number of quanta from the spark, and R_{NH_3} and R_H are the respective rates of conversion by ammonia and atomic hydrogen.

Table 1.

Press. NH_3	Press. p-H_2	R_H	R_{NH_3}	Spark hv	$d[H_{NH_3}^*]/dt$	γ
30	50	.0437	.1521	$1.79\ 10^{16}$	$1.99\ 10^{15}$	0.53
29	52	.0253	.0548	$7.97\ 10^{15}$	$1.99\ 10^{15}$	0.66
29	51	.0253	.0478	$6.08\ 10^{15}$	$1.99\ 10^{15}$	0.68
29	52	.0285	.0343	$5.01\ 10^{15}$	$1.99\ 10^{15}$	0.50
31	50	.0427	.0577	$5.76\ 10^{15}$	$1.99\ 10^{15}$	0.48
30	52	.0343	.0352	$3.17\ 10^{15}$	$1.99\ 10^{15}$	0.65
m.m.	m.m.	$d\log\left(\frac{u_t}{u_o}\right)/dt$		hv/sec/10^2 c.c.	atoms/sec/10^2 c.c.	Mean 0.58

Since the rate of production of atomic hydrogen, against which was compared the rate of conversion by ammonia sensitisation, was measured absolutely, the value of ·58 for the quantum efficiency of the primary process is absolute.

Life of Amine Radicals.

In the photolysis of ammonia the concentration of hydrogen atoms and their life, as well as the nature and proportions of the end products, of which nitrogen is undoubtedly one, have all been subjected to close investigation. Owing to the difficulties of technique, little or no data have been obtained for amine radicals. The interaction of amine radicals must account for the formation of nitrogen and any hydrazine in the end products. In the present work it has been attempted to measure the life of amine radicals from which much useful information could be obtained about the role of nitrogen in the photolysis.

With the existing apparatus the simplest method of determining the life of amine radicals was to make use of the atomic hydrogen inhibition of the ammonia photolysis and interpose a rotating sector between the radiation sources. Since, however, a rotating sector reduces the intensities incident on the reaction vessel, both by its rotation and by the unavoidably increased distances between the radiation sources and the vessel, a modified sector was designed in the form of a cylinder.

This design, when used with a cylindrical reaction vessel, reduced the intensity loss of increased spacing and at the same time had the further advantage of permitting a smaller interval between exposures to the sources. The smaller interval is due not to increase in the possible rotation speed, but to the possible decrease in the angle of the arc separating the sources. With a disc this angle cannot generally be less than 180°, but with a cylinder it can be less than 90° if necessary.

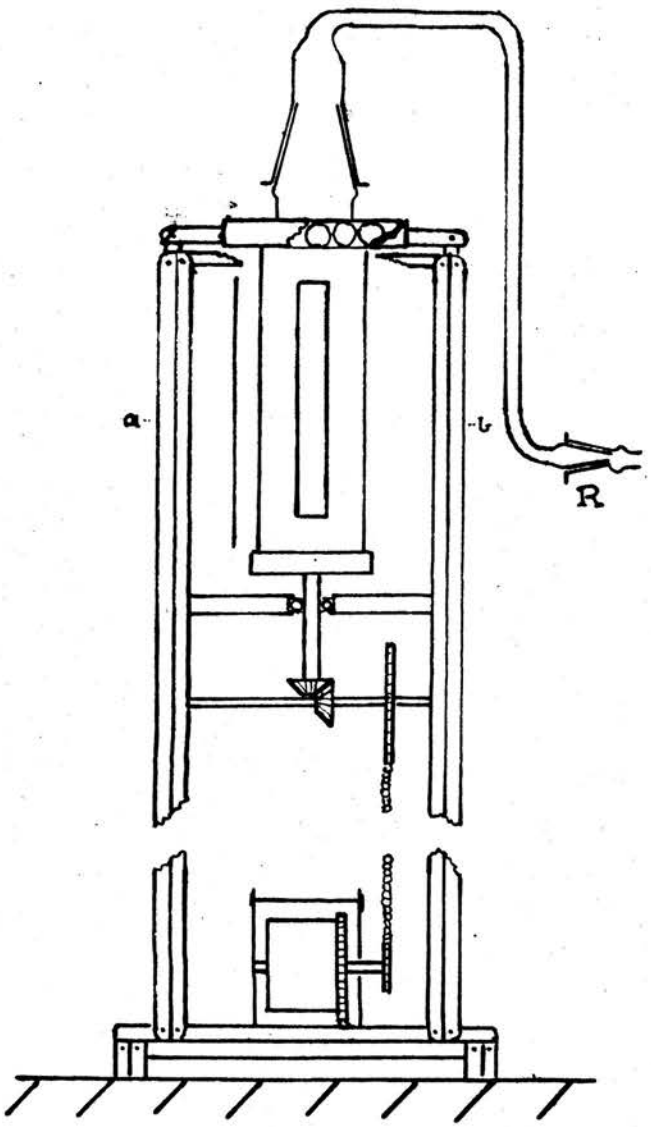
The most probable explanation of the atomic hydrogen inhibition of the ammonia photolysis is acceleration of the back reaction of the primary process

$$NH_2 + H \rightarrow NH_3$$

This reaction therefore provides a means of determining the life of an amine radical. When a slotted cylinder is rotated and the enclosed reaction vessel is exposed alternately to a zinc spark and a mercury discharge lamp, ammonia and hydrogen in the vessel are dissociated alternately. As the slot passes the spark radiation, ammonia dissociates

$$NH_3 + h\nu \rightarrow NH_2 + H$$

and as it passes the discharge lamp hydrogen dissociates



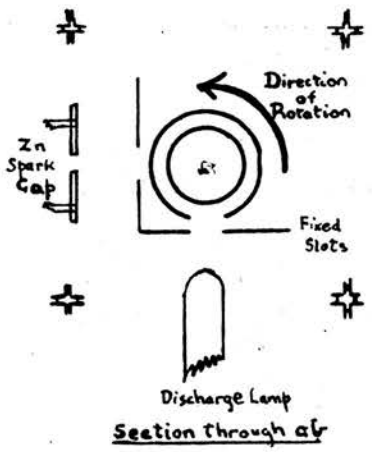


Fig. 1. Cylindrical Rotating Sector

$$H_2 + Hg^* \rightarrow H + H + Hg$$

If the amine radicals have not decomposed in the interval between the exposures to the two sources, inhibition of the ammonia photolysis will be observed. On the other hand, if they have decomposed, no inhibition will occur. By finding the interval between exposures which gives a just appreciable inhibition, the life of amine radicals should be determinable.

Since it was expected that amine radicals would have a life comparable to that of hydrogen atoms (i.e. 10^{-2}-10^{-3} seconds), an apparatus was designed and constructed to permit of a cylindrical sector being rotated by an electric motor at speeds up to 2-3000 revs/min. Figure 1 shows the details of the design. The angle iron members of the frame were Meccano products. The frame proved adequately rigid even at the highest rotation speeds. Later it was found necessary to reduce the speed of rotation below the critical limit of the electric motor and reduction gearing was introduced. At first a 6/1 reduction was used which permitted of a rotation speed as low as 40 revs/min. but further reduction proved necessary. This was obtained by driving the cylinder by a universal electric

motor through the gearing of a springless gramophone motor. The drive was taken from the motor by friction to the governor plate of the gramophone motor and then by Meccano chain transmission to the cylinder. By potentiometer voltage control of the motor and by the governor control of the gramophone motor, a very steady variable rotation speed of ½-1 rev/min. could be obtained at the prime sprocket of the chain transmission. Further control of the speed was obtained by varying the sprocket wheel ratios.

The source of 2537° A radiation was an argon-mercury discharge lamp of the type described by Melville. These lamps are particularly suitable for this work on account of their self starting property, constancy of output and high proportion (greater than 90%) of intensity in the 2537° A line. A further advantage is the absence of broadening of the 2537° A line. Short wave radiation ca. 2000° A was obtained from an air cooled zinc spark operated in the same conditions as described on page 85 . The decomposition of ammonia was the measure of the inhibition and was determined by observing the rate of production of non-condensable gas on a Pirani gauge. Since the constancy of inten-

sity of a spark cannot be safely assumed from exposure to exposure, a photometer was constructed. It consisted of a cylindrical silica cell connected through a U-tube to a Pirani gauge. The cell was place behind the spark gap and a slit arrangement regulated the intensity falling upon it. Ammonia at a pressure of about 50 m.m. was exposed in the cell to the spark and the extent of decomposition, as measured on the Pirani gauge, provided a means of checking the constancy of the spark intensity. Any small deviation from exposure to exposure was corrected by the photometer readings. The intensity of the discharge tube was assumed to be constant for a given current.

The experimental procedure was to introduce about 3 m.m. of ammonia, which was frozen out, and 0.25 m.m. of hydrogen to the reaction vessel. The pressure of hydrogen was measured on the Pirani gauge. With the cylinder sector rotating at the desired speed, the reactants were exposed to the radiation from the mercury discharge lamp, and the increase of non-condensable gas measured on the Pirani gauge. The exposure was repeated with the spark radiation alone and the increase of non-condensable gas measured again. Finally, the

same exposure was given with both the spark and discharge lamp radiating and the non-condensable gas increase noted. The output of the discharge lamp was considered to be constant for the purposes of these experiments. The spark was checked for constancy by the photometer and any correction necessary applied. Two methods were adopted to time the rotation speed according to the speed in question. At high speed, 1000-2000 revs/ min., the revolutions were counted with a revolution counter in contact with the motor armature shaft and timed with a stop watch. The retardation due to the power absorbed when the counter was brought into contact was probably less than 10%. At slow speeds, $<$40 revs/min., revolutions were counted at intervals during the exposures by direct observation and timed by stop watch. At very slow speed (ca. 1 rev/min), every revolution during the timed exposure was counted and every other revolution timed as an intermediate check on the constancy. Reference marks were made on the cylinder and frame to facilitate counting. Inhibition over a range of slot intervals is tabulated in Table 1.

Table 1.

Time of Exposure	Slot Interval	Pressure NH₃	Pressure H₂	Press. n.c. Gas Produced A	Produced S	Produced SA	Photometer S	Photometer SA	Ratio S/(SA-A)
10	$7.5\ 10^{-2}$	4.0	.386	.006	.031	.023	-	-	1.82
10	$7.5\ 10^{-2}$	4.0	.372	.002	.028	.020	-	-	1.56
10	$1.6\ 10^{-1}$	4.6	.296	.001	.019	.014	-	-	1.46
10	$3.8\ 10^{-1}$	5.5	.273	.003	.028	.025	-	-	1.27
15	4.6	3.3	.239	.003	.026	.018	.119	.089	1.30
15	4.5	3.8	.234	.006	.040	.036	.221	.246	1.48
15	4.5	3.8	.234	.003	.045	.028	.370	.266	1.30
10	5.0	3.1	.307	.003	.015	.011	-	-	1.89
15	10.0	3.9	.240	.006	.086	.110	.592	.726	1.02
15	10.0	3.9	.240	.006	.036	.043	.216	.358	1.61
15	10.0	4.0	.240	.006	.035	.030	.166	.158	1.39
15	10.0	3.7	.240	.001	.023	.014	.077	.076	1.47
20	10.3	3.5	.299	.005	.050	.048	-	-	1.16
20	14.9	3.7	.295	.010	.056	.053	-	-	1.30
15	14.9	4.0	.240	.005	.024	.017	.067	.067	2.00
15	20.0	4.0	.240	.004	.034	.037	.148	.148	1.03
20	19.7	4.0	.289	.007	.064	.063	-	-	1.16
16	27.0	4.3	.272	.009	.055	.048	-	-	1.40
18	30.0	4.0	.275	.007	.025	.022	-	-	1.66
20	30.0	4.0	.296	.005	.018	.031	-	-	0.69
20	29.7	4.0	.313	.007	.032	.036	-	-	1.10
16	30.0	3.7	.240	.006	.024	.030	.109	.124	1.18
16	30.0	3.7	.240	.005	.031	.028	.118	.110	1.26
16	30.0	3.3	.240	.008	.022	.023	.102	.088	1.26
16	50.0	3.9	.240	.005	.024	.017	.108	.090	1.67
20	75.0	4.0	.240	.005	.032	.027	.148	.164	1.41
20	72.0	4.0	.240	.007	.030	.024	.133	.130	1.74
20	72.0	3.4	.240	.008	.042	.037	.144	.142	1.59
min.	sec.	m.m.	m.m.	m.m.	m.m.	m.m.	$V^2-V_o^2$		

Reaction Volume = 100 c.c.

Temp. = 20° C. 2537° A = ca. $3.38\ 10^{13}$ hv/sec. Spark = ca. $9.68\ 10^{12}$ hv/sec

From the fact that S/(S-A) is always greater than unity, it is apparent that inhibition persists even when the interval between exposure to spark and discharge lamp is 70 seconds. The discussion of the significance of this persistence is postponed to the General Discussion (page135).

It might be thought an appreciable error is introduced to the measurement of the non-condensable gas pressure increase by using the Pirani calibration for hydrogen. This calibration was satisfactorily linear up to 0.4 m.m. At the most the pressure increase due to non-condensable produced was 0.160 m.m. Of this, only 0.040 m.m. was nitrogen and since the total pressure of nitrogen and hydrogen was about 0.4 m.m., the percentage of nitrogen did not exceed 10% and, in fact, it generally amounted to less than 5%. The heat loss by the wire by thermal conductance through nitrogen and hydrogen can be expressed

$$V_{N_2}^2 = k K_N p$$

$$V_{H_2}^2 = k K_H (1-p)$$

where K_N and K_H are the thermal conductivities of nitrogen and hydrogen and p is the fraction of nitrogen in the gas. The fractional heat loss due to nitrogen is therefore

$$\frac{V_{N_2}^2}{V_{H_2}^2 + V_{N_2}^2} = \frac{K_N p}{K_N p + K_H (1-p)}$$

$$= \frac{5.24\ 10^{-5} \cdot 0.1}{5.24\ 10^{-5} + 3.18\ 10^{-4}\ 0.9}$$

$$= 1.9\ 10^{-2}$$

Thus the loss of heat due to nitrogen was at the most

2% and was generally less than 0.9%. In comparison with the other sources of error, the effect of nitrogen on the linear calibration of the Pirani gauge was negligible.

Primary Mechanism of Hydrazine Photolysis.

As in the mercury sensitised decomposition of hydrazine, the two probable primary processes in the direct decomposition are dissociation at the N-N link and at a N-H link, viz.

$$N_2H_4 \rightarrow NH_2 + NH_2 \quad \ldots\ldots\ldots (1)$$

$$N_2H_4 \rightarrow N_2H_3 + H \quad \ldots\ldots\ldots (2)$$

Here, however, a distinction should be possible since (2) involves the production of atomic hydrogen which can be detected by the para hydrogen conversion. (In the mercury sensitised decomposition the excited mercury atoms themselves would convert the para hydrogen). But there is one serious difficulty in the fact that hydrazine is quite an efficient inhibitor of the para hydrogen conversion (page 43). Since the activation energy of the reaction of atomic hydrogen with hydrazine is comparable with that of the para hydrogen conversion, it is of little advantage working at high temperatures. The addition of 10 m.m. of hydrazine

to 50 m.m. of para hydrogen reduced the mercury sensitised stationary hydrogen atom concentration by a factor of twenty. Thus, even if the primary process in the direct photolysis of hydrazine is unity, a high intensity of radiation from the spark source will be necessary. In Table (1) are tabulated para hydrogen conversion runs in which hydrazine was the sensitising agent.

Table 1.

Exp. Time	%p-H_2	Press. N_2H_4 gas.	$\Delta p_{N_2H_4}$	Corrected % p-H_2	Spark Quanta	Press. N_2H_4
0.0	63.3	54.0	-	63.3	2.95 10^{15}	9.5
30.0	63.4	54.4	1.1	64.1		
0.0	63.3	53.6	-	63.3	3.38 10^{15}	5.3
30.0	62.7	54.1	1.2	63.5		
0.0	63.3	54.0	-	63.3	2.51 10^{15}	8.6
30.0	62.5	54.2	0.9	63.2		
0.0	63.3	54.4	-	63.3	2.11 10^{15}	3.3
30.0	62.6	54.4	0.9	63.2		
0.0	63.3	56.0	-	63.3	2.11 10^{15}	3.0
30.0	62.6	56.0	0.7	63.0		
min.		m.m.	m.m.		hv/sec.	m.m.

Reaction Volume = 100 c.c. Temp. = 20° C.

Notes on Table 1.

1. In the second column, %p-H_2 is corrected by the usual equilibration method for nitrogen produced in the reaction (page 24).

2. $\Delta p_{n.c.}$ was computed in a similar manner to that in the collision efficiency experiments (page 61).

3. Spark quanta have been calculated from the amount of non-condensable gas produced on the basis of a quantum efficiency of 1.2 (Welge & Beckmann)[8] for the hydrazine photolysis.

From these data it is impossible to say which is the mechanism of the primary process, the conversions observed are all too close to the experimental error. The water bath surrounding the reaction vessel in these experiments limited the possible intensity.

General Discussion.

Before reviewing the bearing of the new results from the present work on the ammonia photolysis, a resumé of the existing knowledge must be made. A repetition of certain facts mentioned previously is unavoidable but it is intended to treat them more quantitatively and in more detail. The existing experimental observations of which account must be taken in any attempt at explaining the mechanism of the ammonia photolysis, whatever the perspective adopted, are the following:-

(1) The absorption spectrum of ammonia in the region 2250-1800° A is wholly diffuse bands and even at the lowest pressure no fluorescence ( ) of the ammonia molecule has been detected. These facts are in accordance with a predissociation process involving a very rapid disruption of the molecule (10^{-13} seconds) as the primary process of the photolysis. A quantum efficiency of unity for this process is implicitly assumed. The repulsive state produced by the absorption of a quantum may lead to dissociation

by (a) $NH_3 + h\nu \rightarrow NH_2 + H$

or by (b) $NH_3 + h\nu \rightarrow NH + H_2$

But for the fact that electronic selection rules rather favour it, reaction (b) could almost be ruled out by the extreme difficulty which it introduces in accounting for the secondary reactions in the overall decomposition.

(2) The final products of the photolysis in a static system are nitrogen, hydrogen and perhaps traces of hydrazine.[6,11] Atomic hydrogen has been definitely established as an intermediate product.[7] Indirect evidence for amine radicals has been deduced from the decomposition of liquid ammonia by alkali metals into hydrogen and amide ions.[32] The most important determination of the nitrogen-hydrogen ratio has been made by Welge and Beckmann.[8] Approaching zero decomposition, these authors found that this ratio tended to 100% hydrogen. At the same time the quantum efficiency approached unity. Their results are summarised in Table (1).

Welge and Beckmann's Results
for
The Quantum Efficiency and Ratio H_2-N_2 in Photolysis of Ammonia ($\lambda = 1990^0$ A).

Pressure NH_3 m.m.	Time min.	Pressure Products m.m. 10^{-4}	% H_2 in Products	NH_3 Molecules Decomposed 10^{14}	Quanta Absorbed 10^{14}	Quantum Yield
2.2	29.5	4.2	94.5	39.45	46.55	0.85
5.9	28	5.65	96.8	57.5	61.25	0.94
6.0	29	6.37	96.8	64.75	68.37	0.95
13.8	18	4.63	92.67	40.95	51.95	0.79
14.3	29	8.2	95.5	80.15	85.78	0.94
29.3	23	6.4	94.45	60.2	69.55	0.87
30.0	18.5	5.0	95.6	49.03	54.55	0.90
60.7	19.5	4.46	94.1	41.4	55.77	0.74
128.2	29.5	8.7	90.5	70.2	81.9	0.86
					Aver.	0.87

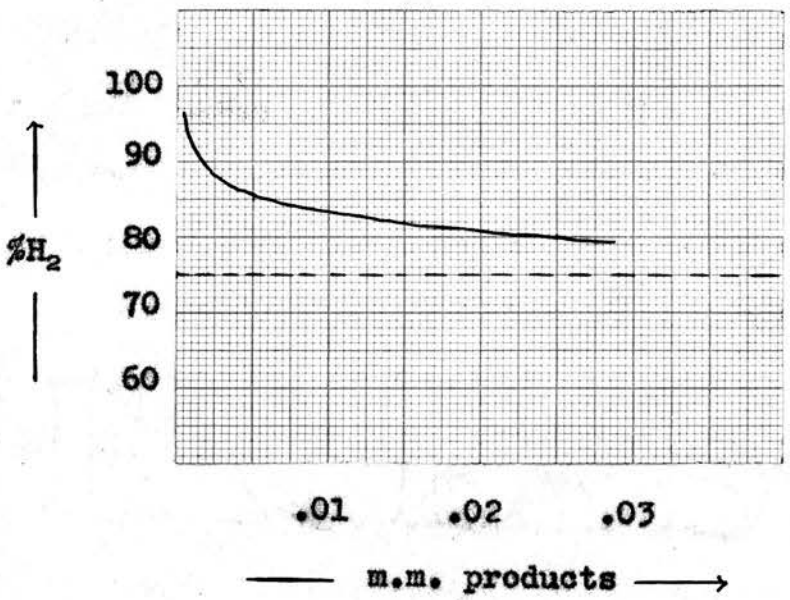


Fig. 1. Variation in cpmposition of products with the extent of the ammonia photolysis. (Welge and Beckmann.)

It will be observed that the nitrogen-hydrogen ratio is independent of pressure as is the quantum efficiency. The value of the quantum efficiency obtained is dependent on the analysis of the products. If the data were calculated on the basis that hydrogen was 75% of the non-condensable products, the quantum efficiency would be approximately 0.25. This is due to the fact that by the stoichiometric equation,

$$N_{NH_3} = 6\,(f - 0.667)\,N\,\frac{pV}{RT}$$

(where f = mole fraction of hydrogen, N is Avogadro's number, p is pressure of products and V = volume of reaction vessel) four times as many ammonia molecules are decomposed if the mole fraction of hydrogen is unity (100%) than when it is 75%. The variation of f with p is given in Fig. (1). The value of f does not reach the limiting value of 0.75 till about 0.05 m.m. of products are produced. The relation is independent of ammonia pressure over at least 4-20 m.m. It may be noted, however, that Wiig & Kistiakowsky[33] found that the stoichiometric ratio for nitrogen and hydrogen held down to 0.008 m.m. of non-condensable products in their reaction vessel. At about 0.002 m.m. of products, Wiig[34] observed indirect evidence in the γ-pressure relation

of a change in composition in the direction of increasing hydrogen. The ratio of nitrogen and hydrogen at greater extents of decomposition has been determined by several workers whose results are summarised in Table (2).

Table 2.

H_2-N_2 Ratio Determinations
(Adapted from Welge & Beckmann)[8].

Date	Investigator	NH_3 Pressure	Minimum Products for Anal.	$\%H_2$	Analysis Method
1926	Dickinson & Mitchell [35]	0-1	5	87	
1927	Bates & Taylor [36]	-	40	96	Chemical
1932	Wiig & Kistiakowsky	0-760	15	75	McLeod-Pirani
1934	Ogg, Leighton & Bergstrom [33]	1-9	large	75	Chemical
1935	Wiig [34]	0-900 m.m.	20 m.m. 10^3	75	McLeod-Pirani

The early values of $\%H_2$ in excess of the stoichiometric yield are accountable by the fact that hydrogen-nitrogen mixtures separate easily, hydrogen with its higher diffusion rate tending to outpace nitrogen when a nitrogen-hydrogen mixture is moved. Thus analyses of samples removed from a mixture tend to be high in hydrogen. This has been observed by several workers including Wing & Kistiakowsky, Wiig, and also the present

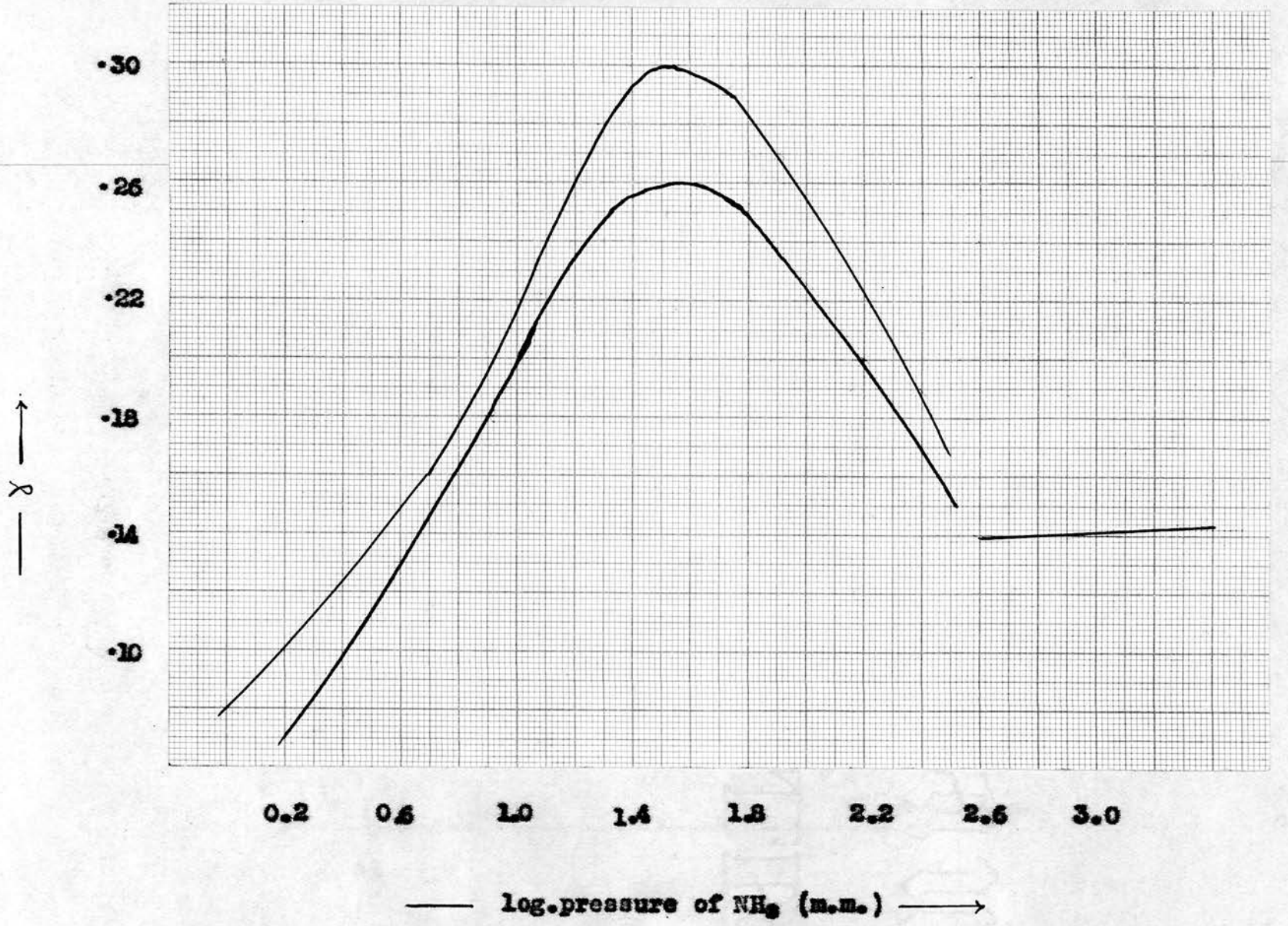


Fig. 2. Pressure dependence of the quantum efficiency of the ammonia photolysis.

worker (page 21). It is therefore fairly safe to take the stoichiometric value of 75% hydrogen as the limiting value of the nitrogen-hydrogen ratio.

(3) The pressure dependence of the quantum efficiency has been determined by Wiig[13,14] and Ogg, Leighton and Bergstrom.[14] The former covered the pressure range 0.75 m.m. to 886 m.m., and the latter 912 m.m. to 6500 m.m. Their results are given graphically in Fig. (2). A definite maximum efficiency is observable about 100 m.m. The magnitude of this maximum may be dependent to a certain extent on the size of the reaction vessel, as is shown by the two curves. The upper curve was obtained with a reaction vessel of 99 c.c. capacity and a volume-area ratio of 200 $m.m.^{-1}$ The lower refers to a reaction vessel of 44.5 c.c. capacity and an area volume ratio of 157 $m.m.^{-1}$ In the region 912-6500 m.m., determined by Ogg, Leighton and Bergstrom, the quantum efficiency is practically constant.

(4) The occurrence of hydrogen atoms as an intermediate product of the ammonia photolysis has been clearly established by several investigators and particularly by Farkas and Harteck.[7] Their measurements of the stationary concentrations of atomic hydrogen in different conditions have already been

summarised fully (page 79). It will suffice to repeat here that on the assumption of an invariable quantum efficiency of unity for the primary process, they conclude that the atomic hydrogen concentration is low at room temperature and normal at about 300° C. The factor of abnormality is between two and six over a pressure range of 30 to 1 m.m. ammonia. Since the atomic hydrogen concentration is measured by para hydrogen conversion, the factor is subject to the accuracy of the velocity constant (k^*) of the conversion. The values of k^* given by Farkas[29] and by Geib and Harteck[5] show a marked difference at low temperatures and only a fair agreement at high temperatures (page67). In Table 3 are compared the values of k computed by Farkas and Harteck[7] from E = 7000 k cals. with those of Farkas and of Geib and Harteck.

Table 3.

Temp.	$\frac{10^3}{T}$	Value of k^*		
		Farkas & Harteck	Farkas	Geib & Harteck
19	3.43	$1.95\ 10^5$	$9.33\ 10^5$	$1.41\ 10^5$
100	2.68	$3.08\ 10^6$	$1.00\ 10^7$	$2.75\ 10^6$
200	2.12	$2.50\ 10^7$	$6.00\ 10^7$	$2.51\ 10^7$
300	1.75	$1.03\ 10^8$	$1.95\ 10^8$	$1.01\ 10^8$
400	1.49	$2.80\ 10^8$	$4.47\ 10^8$	$3.02\ 10^8$
°C.		moles^{-1} litre sec.$^{-1}$		

It will be observed that Farkas's value, an experimental one, for k^* at 300° C. is 1.9 times that (an

extrapolated value) of Geib and Harteck. Thus, considering the uncertainty of the data for k^*, the reality of a small factor of abnormality is open to a certain amount of doubt.

(5) The inhibition of the direct photodecomposition of ammonia by atomic hydrogen is the best evidence for the existence of reversal of the primary dissociation

$$NH_2 + H \rightarrow NH_3$$

Being a low pressure phenomenon occurring at least partly on the walls it is not amenable to rigorous quantitative treatment. When the intensities of the spark and 2537° A radiation are about the same, the direct photodecomposition rate of 3 m.m. ammonia is cut down by $\frac{1}{3}$ to $\frac{1}{2}$ in the presence of 0.3 m.m. hydrogen. It has been suggested that this inhibition is due to regeneration of ammonia by the reaction of atomic hydrogen with hydrazine (Mund, Taylor and others)[12,37]

$$H + N_2H_4 \rightarrow NH_3 + \tfrac{1}{2}N_2 + H_2$$

and both mechanisms have been advanced as an explanation of the concomitant experiment of Jungers and Taylor in which exchange between atomic deuterium and ammonia was observed. These authors exposed 600 m.m. deuterium and 160 m.m. ammonia to the radiation of

2100° A and 2537° A for 48 hours and found the deuterium content of the ammonia to be 70%. When exposed to 2537° A alone for 72 hours the deuterium content was only 1% (the pressure of deuterium was sufficient to inhibit the mercury sensitised decomposition). Thus atomic deuterium cannot exchange with ammonia at ordinary temperatures unless the ammonia is photodecomposing. This fact could be interpreted by either of the suggested inhibition mechanisms.

(6) Gedye and Rideal[10] have determined the yield of hydrazine from photodecomposing ammonia in a flow system. Their data are summarised in Table (4).

Table 4.

Mean Flow Rate	Reaction Vessel Temp.	N_2H_4 Produced as % NH_3 Decomposed
63	45	23.1
43	"	21.6
8	"	0.9
76	120	4.8
74	"	4.4
8	"	0.4
80	11	55.7
70	2	57.2
8	11	31.0
c.c./min.	° C.	

It will be observed that the yield of hydrazine is dependent (a) on the temperature, and (b) on the rate

of flow. The dependence of (b) is linked to (a) since the products were cooled by passing through a water jacketed capillary at the exit from the reaction vessel. This is confirmed by the experiments at 11° C. where the hydrazine yield is very much less dependent on the rate of flow. It is, however, this remaining dependence on rate of removal from the reaction zone which must account for the very small traces found in static systems by Koenig & Brings[11] and Welge & Beckmann.[8]

Ogg, Leighton & Bergstrom[14] have determined the quantum efficiency of hydrazine decomposition when 3000 m.m. ammonia and 8 m.m. hydrazine are exposed to 2140° A radiation. They find that ammonia absorbs nearly all the radiation (94.5%) but since the products are equiproportions of nitrogen and hydrogen, they conclude that hydrazine alone has decomposed according to Elgin and Taylor's[17] stoichiometric equation

$$2\ N_2H_4 = 2\ NH_3 + N_2 + H_2$$

On this basis they compute the quantum efficiency of the ammonia sensitised decomposition of hydrazine and obtain 1.3 on total quanta absorbed. This has been taken (P.A. Leighton)[16] to be the quantum efficiency of

$$H + N_2H_4 \rightarrow NH_3 + NH_2$$

"and a reaction involving amine radicals and hydrazine must follow in order to account for the observed quantum yield of more than unity". If this is so it is difficult to explain the observed nitrogen-hydrogen ratio of unity by any mechanism, but a complex one

$$2\ NH_2 + N_2H_4 \rightarrow 2\ NH_3 + N_2 + H_2.$$

The most important theoretical treatment of the ammonia photolysis is that of Mund and van Tiggelen. They introduced hydrazine into the reaction mechanism in an attempt to explain qualitatively (a) the low concentration of atomic hydrogen at room temperature, (b) the low quantum efficiency, (c) the hydrogen rich analyses of the non-condensable products made by Welge and Beckmann, (d) the observed dependence of the quantum efficiency on pressure, (e) the formation of deutero-ammonias by exchange with photo-decomposing ammonia, and (f) the increase in quantum efficiency with increase in rate of decomposition reported by Mund.[15] Of these, only (b) is capable of semiquantitative treatment by the existing data. Mund and van Tiggelen have deduced the following equation for this dependence on the basis of the reaction mechanism on page 12 and a quantum efficiency of 0.2 at 1 atmosphere

$$\gamma = \frac{1}{0.875 + \sqrt{0.0156 + \sqrt{K\,P/v}}}$$

where v ($\propto I_{Abs.}$) is the reaction velocity (expressed as the ratio of the number of ammonia molecules decomposed to nitrogen and hydrogen per c.c. per second) and P is the total pressure. The observed dependence is in quite good agreement but Leighton[16] has shown (page 13) that a slightly modified scheme gives the same result if he assumes different relative rates of reaction. The necessity of assuming relative reaction rates in a postulated scheme emphasizes the essential empiricism of the observed agreement. And it is perhaps not too dogmatic to say that this is largely true of any attempt to establish quantitatively a reaction mechanism from the pressure dependence of a quantum efficiency. Secondary reactions with hydrazine, however, do provide a good qualitative explanation of the observed facts about the ammonia photolysis, but the reality of (e) has been questioned above.

Summary of New Data.

The new facts upon which attention has been directed in the present work are the following.

(1) The collision efficiency, activation energy and steric factor of the reaction of atomic hydrogen with

hydrazine have been determined and are summarised in Table (5).

Table 5.

	Temp.	Value of k* Farkas	Value of k* Geib & Harteck
Collision Efficiency (pp. 43-69)	205°C.	$4.05\ 10^{-5}$	$1.71\ 10^{-5}$
	91°C.	$3.02\ 10^{-6}$	$9.38\ 10^{-7}$
	23°C.	$4.67\ 10^{-7}$	$7.17\ 10^{-8}$
Activation Energy (pp. 69-70)	-	6.85 k cals	8.64 k cals
Steric Factor (pp. 70-71)	205°C.	$5.51\ 10^{-2}$	$1.38\ 10^{-1}$
	91°C.	$3.98\ 10^{-2}$	$1.45\ 10^{-1}$
	23°C.	$5.33\ 10^{-2}$	$1.76\ 10^{-1}$

The low value of the collision efficiency rules out the possibility of hydrazine being responsible for the low concentration of atomic hydrogen at room temperature reported by Farkas and Harteck.[7] This can be shown by the following consideration. A hydrogen atom in diffusing towards the walls in 10 m.m. of hydrazine would undergo on the average

$$10^{1\sigma} \times \frac{10}{760} \quad \text{collisions/sec}$$

Applying Einstein's diffusion equation

$$x^2 = 2Dt$$

where D is the diffusion coefficient in $cm^2/sec.$, the time taken by the atom to diffuse 1 cm. is 1 second.

Thus a hydrogen atom undergoes $1.32\ 10^{8}$ collisions with hydrazine in diffusing 1 cm. towards the walls. Since the collision efficiency is from $7.17\ 10^{-8}$ to $4.67\ 10^{-7}$, it is apparent that in the presence of 10 m.m. of hydrazine the rate of removal of hydrogen atoms would be comparable with the rate of diffusion to the walls. But when the quantum efficiency of the ammonia photolysis is being determined, the total amount decomposed is at the most 0.1 m.m. and therefore the amount of hydrazine produced during the whole run cannot exceed 0.05 m.m. Even if this hydrazine were present at any given instant, the number of collisions which a hydrogen atom would undergo with it would be $8.69\ 10^{5}$. Thus it is clear that the removal of hydrogen atoms by hydrazine in the ammonia photolysis could not be a faster process than diffusion to the walls. It must be added that this does not conflict with the ammonia sensitised decomposition of hydrazine (Ogg, Leighton & Bengstrom)[14] since in these experiments the hydrazine pressure was 8 m.m. On the basis of the above calculation it will therefore be evident that every hydrogen atom generated from the ammonia will attack hydrazine.

(2) The rate of removal of atomic hydrogen from the

homogeneous phase at room temperature has been found to be no greater than that to be expected by diffusion to the walls and third-body collisions (pp. 79-90).

(3) The quantum efficiency of the reaction of atomic hydrogen with hydrazine has been measured and the value obtained of 0.43 does not support the suggestion that the low quantum efficiency of the ammonia photolysis is due to this reaction. And particularly contradictory is the fact that the ratio of ammonia produced to hydrazine decomposed is not unity as the suggested mechanism would imply, but 0.5. It must be pointed out that the former determination is very probably low for a variety of causes, but the latter is independent of these causes (pp. 30-42).

(4) The quantum efficiency of the primary process has been found to be 0.58 by direct measurement (pp. 99-102).

(5) The life of amine radicals has been established as greater than 75 seconds. The life of hydrogen atoms at 15 m.m. hydrogen pressure in the same reaction vessel was $1.65\ 10^{-3}$ - $1.09\ 10^{-1}$ seconds (pp. 91-98 and pp. 103-111).

Interpretation of Old and New Data.

In the foregoing, a number of new facts about the

kinetics of the ammonia photolysis have been established and a resumé has been made of those which have been established in a large number of researches. It now remains to correlate them.

The first important question is the nature and efficiency of the primary mechanism. The predissociation hypothesis is undoubtedly the correct qualitative interpretation of the spectroscopic evidence but it cannot establish the exact efficiency of the primary mechanism. By the method detailed above it has been shown that at room temperature and pressures of the order of 100 m.m., this efficiency is only 0.58. This fact immediately accounts at least partly for the low quantum yield of the overall reaction. It has already been mentioned that ammonia exhibits no fluorescence even at as low a pressure as 0.007 m.m. (Bonhoeffer and Farkas)[3] and therefore the energy acquired by the ammonia molecule must be dissipated in some other manner. There are only two ways in which this can be done. The first is by collision with the other molecules in the reaction system. The second is by so-called internal degradation. The latter process is always possible in a polyatomic molecule, and really involves the excitation of one or more of the vibration-

al modes of motion of the molecule at the expense of the electronic energy. For such a conversion of energy to occur efficiently, as it apparently does in the case of ammonia, the vibrational modes must be capable of absorbing all the electronic energy. These modes are normally sharply quantised in simple molecules but in polyatomic molecules the energy levels are somewhat broader and the process is more likely to occur.

Although the efficiency of the primary process has not been measured over a wide pressure range (the method adopted precludes this to some extent) the fact that the overall quantum efficiency does not vary greatly with pressure would tend to indicate that deactivation is not a collision process. The second process, of internal degradation, would probably be unaffected by pressure, except at very high pressures, and would therefore be more consistent with the observations.

This method of measuring the efficiency of the primary mechanism by para hydrogen conversion also excludes dissociation into NH and H_2, since neither of these molecules would convert para hydrogen at the rate

observed in these experiments.

Nothing has been said about the effect of temperature on the primary process. The overall quantum efficiency of the ammonia decomposition does increase with temperature, and it is therefore a question for the future to decide whether this increase is due to the primary or the secondary mechanisms.

Having obtained the rate at which hydrogen atoms are produced, the next question is how they disappear. The experiments described above (page 79) have shown quantitatively that these atoms disappear at a normal rate, i.e. there is no important reaction, due to the decomposition of ammonia, competing with the normal processes of removal by combination in the homogeneous phase and at the walls. But we have seen that although the primary efficiency is low (0.58) it is not low enough to account for the low overall efficiency of 0.3 at the same pressure. Thus ammonia must be regenerated by some secondary reaction, because this has been proved by inhibition of the direct decomposition by atomic hydrogen and also quantitatively by the exchange technique. A fraction of the hydrogen atoms must be used in this process. Although the removal of the fraction

does not appreciably affect the stationary atom concentration, yet the rate of regeneration of ammonia must be of the same order of magnitude as the combination of the hydrogen atoms and, moreover, must vary in much the same way with conditions such as pressure and temperature.

In order to account for the regeneration of ammonia, we have seen that it has been suggested that atomic hydrogen attacked hydrazine formed by combination of amine radicals. This process must be eliminated because it has already been shown (page 126) that the hydrazine concentration cannot build up under static conditions to such a value as would allow this process to play an important role in the ammonia photolysis. Another objection to the hydrazine mechanism is that when hydrazine is attacked by hydrogen atoms the following reaction presumably occurs

$$H + N_2H_4 \rightarrow NH_3 + NH_2$$

According to this mechanism, amine radicals are produced once more and continue to form hydrazine which in turn is attacked. Thus no nitrogen and hydrogen would be produced. It has been suggested that the following complex reaction would result in the eventual production of nitrogen and hydrogen

$$2\ NH_2 + N_2H_4 = 2\ NH_3 + N_2 + H_2$$

There is absolutely no evidence for the existence of such a reaction. That hydrazine is formed must be accepted beyond doubt. The real point at issue is the amount. Hydrazine was introduced into the reaction mechanism mainly to account for the low hydrogen atom concentration. We have seen that this is no longer necessary and therefore we must seek a reaction mechanism involving amine radicals instead of hydrazine.

Here a difficulty is encountered. If the results are interpreted on the basis of the reaction

$$H + NH_2 \rightarrow NH_3 \qquad (2)$$

and that moreover this reaction has to compete with

$$H + H \rightarrow H_2 \qquad (3)$$

and also with

$$NH_2 + NH_2 \rightarrow N_2 + 2H_2 \qquad (4)$$

the latter of which is responsible for the production of some hydrogen and all the nitrogen, then the stationary concentration of amine, and therefore its lifetime, must be comparable with that of hydrogen atoms. But by employing the inhibition technique, it has been shown that the lifetime of the entity which is responsible for ammonia regeneration, that is ex

hypothesi NH_2 radicals, is more than 1000 times that of hydrogen atoms. This might be taken at once to imply that the product of the reaction must be hydrazine since no free radical could possibly have such a long lifetime. This, however, is ruled out from another consideration altogether. There is no doubt that at room temperature this entity does eventually decompose in absence of radiation and therefore of hydrogen atoms. But hydrazine is absolutely stable (vide page 54), measurable decomposition commencing only at 200° C. Further, it may be added that in Gedye and Rideal's experiments the yield of hydrazine was much reduced on raising the temperature of the system to a value at which hydrazine does not decompose. Whatever this entity may be, it does not possess the properties of hydrazine. The formation of hydrazine is not, of course, excluded by postulating reaction (4). It is merely implied that in a static system the majority of amine radicals react in this way. In a flow system such as used by Gedye and Rideal, which incorporates a liquid oxygen trap to collect the hydrazine, the amine radicals are removed so rapidly that the probability of their forming hydrazine is enormously increased.

The long apparent lifetime of the amine radical would, however, appear to give the clue to this anomaly. It could not be imagined that such a radical can exist in the gas phase for a time of the order of 10^{-3} seconds. Therefore it must diffuse to the walls and remain there for this period. Now at high ammonia pressures it might be thought that the probability of amine radicals getting to the walls would be absolutely negligible and that therefore any surface reaction could be eliminated. It must be remembered however that the extinction coefficient of ammonia increases with pressure with the result that the zone of reaction moves closer and closer to the walls. The probability of amine radicals getting to the walls is thus unaffected by ammonia pressure. The same argument applies to hydrogen atoms and may be illustrated in the following manner. The extinction coefficient of ammonia for 2144° A has been measured by Bacon and Duncan who find that a 8 m.m. layer of ammonia at 40 m.m. pressure absorbs about 50% of radiation of that wavelength. At a high ammonia pressure such as 8 atmospheres 50% of the radiation will be absorbed in a layer $5.3\ 10^{-3}$ $\left(= \frac{.8 \times 40}{8 \times 760}\right)$ cm. wide. The diffusion coefficient of a hydrogen atom in ammonia at this pressure can be computed from Jeans'[38] equation

$$D = \frac{K}{p_x(\sigma_H + \sigma_{NH_3})} \left(\frac{1}{M_H} + \frac{1}{M_{NH_3}}\right)^{\frac{1}{2}} \quad \ldots\ldots\ldots(1)$$

where K is a constant (= 760 7.02 10^{-16}) and σ and M are the molecular radii and masses, respectively. Taking the values 1.07° A and 1.43° A for the respective radii of atomic hydrogen and ammonia, we obtain the value 0.14 for D. Thus in diffusing 5.3 10 cms. a hydrogen atom will take 10^{-4} $\left(= \frac{(5.3\ 10^{-3})^2}{0.28}\right)$ seconds. In that time it will undergo, on the average, 8 10^6 collisions with ammonia molecules. The probability of colliding with another atom or radical is therefore extremely small since, even though concentrated in a narrow zone near the walls, the stationary concentration of these will generally not be greater than 10^{-3} m.m. Now at 40 m.m. ammonia pressure the diffusion coefficient of a hydrogen atom is by (1) about 20 and consequently a hydrogen atom will diffuse 8 m.m. in 1.6 10^{-2} seconds and will undergo 3.3 10^6 collisions with ammonia. The probability of hydrogen atoms and amine radicals reaching the walls is thus largely independent of pressure.

The mechanism of the secondary reactions can be depicted in the following way. Ammonia dissociated into amine radicals and hydrogen atoms which diffuse to

the walls and are adsorbed there. The hydrogen atoms quickly, i.e. within 10^{-3} seconds combine either with each other or with amine radicals. The relative probability of the two reactions will, of course, determine the overall quantum yield of the reaction. The ratio will be unpredictable as it will depend on a purely heterogeneous reaction about which nothing is known.

Once the initially produced hydrogen atoms have reacted (and for the moment assuming no more are produced) the amine radicals slowly interact to form nitrogen and hydrogen. If, however, more hydrogen atoms are produced as in the rotating cylinder experiments, these remaining amine radicals will be reduced to ammonia again. The ammonia evaporates from the surface and leaves it ready to adsorb fresh amine radicals. This dual character of the secondary reactions is not an ad hoc postulation since it is directly supported by the measurements of the lifetime of the two reacting intermediates.

We may therefore summarise by writing down the following simple reaction scheme for the ammonia photolysis

$NH_3 + h\nu \rightarrow NH_2 + H$ $\quad \gamma_p = 0.58$ (1)

$H + H \rightarrow H_2$ (2)

$H + NH_2 \rightarrow NH_3$ (3) Walls

$NH_2 + NH_2 \rightarrow N_2 + 2H_2$ (4)

$\rightarrow N_2H_4$ (small and undetermined)

The relative efficiency of (2) and (3) can be determined in the following way. In a paper by Bolland and Melville,[27] it has been shown that the quantum efficiency of a reaction can be calculated without measuring the quantum input to the system. The method depends on measuring the rate of exchange with deuterium atoms. It has been applied to photodecomposition of phosphine thus,

$PH_3 + h\nu \rightarrow PH_2 + H$ $\quad \gamma_p = 1$ (a)

$H + D_2 \rightarrow HD + D$ (b)

$D + PH_3 \rightarrow PH_2D$ (c)

$D + D \rightarrow D_2$ (d)

The expression obtained is

$$\gamma = \frac{R_{ex}}{R_{ex} + 3.55}$$

where R_{ex} is the ratio of the rates (d)/(c) and γ is the overall quantum efficiency. Now in the ammonia photolysis R_{ex} is simply the ratio of (2)/(3) but γ is not the efficiency of the overall reaction, since the

primary process is inefficient. Hence the observed efficiency must be multiplied by the reciprocal of the primary efficiency and then we may write

$$0.3/0.58 = \frac{(2)/(3)}{(2)/(3) + 3.55}$$

that is to say, the ratio of (2)/(3) is 3.9.

In conclusion it may be pointed out that this new interpretation of the ammonia photolysis explains all the observations (page124) for the explanation of which hydrazine was introduced into the secondary reactions. Comparatively simple, it involves no complex reactions for which there is a complete lack of evidence. It replaces that published in a joint letter to "Nature" by H. W. Melville and the author.[41.] The modification which it represents of the latter interpretation has been necessitated by the subsequent direct determination of the primary efficiency and by the observed lifetime of the amine radicals.

Photolysis of Hydrazine.

So far no mention has been made in this discussion of the hydrazine photolysis. As we have already seen, the spectrum of hydrazine is also a predissociation one and again there are two probable primary modes of dissociation, (a) N-H dissociation, and (b) N-N dissoci-

ation. In addition mode (a) may be accompanied by one of two alternative secondary mechanisms, viz.

(a) N-H Dissociation

$$N_2H_4 + h\nu \rightarrow N_2H_3 + H$$

$$H + N_2H_4 \rightarrow NH_3 + NH_2$$

$$NH_2 + N_2H_3 \rightarrow NH_3 + N_2 + H_2$$

or

$$N_2H_4 + h\nu \rightarrow N_2H_3 + H$$

$$H + N_2H_4 \rightarrow N_2H_3 + H_2$$

$$2N_2H_3 \rightarrow 2NH_3 + N_2$$

On analogy with the corresponding reactions of atomic hydrogen with methane and ethane (vide page 39) the former seems the more probable. The data obtained for this reaction in the present work (viz. quantum efficiency, collision efficiency, activation energy and steric factor) cannot provide a distinction. The employment of the deuterium exchange technique in order to settle this question is complicated by the fact that it is a decomposition with the production of ternary mixtures containing nitrogen. Further it is known that rapid exchange occurs between deuteroammonias and hydrazine. The primary mode (b) of dissociation seems improbable since it must involve a complex

secondary reaction if a quantum efficiency of greater than unity is to be explained

(b) N - N Dissociation

$$N_2H_4 + h\nu \rightarrow 2NH_2$$

$$2NH_2 + N_2H_4 \rightarrow 2NH_3 + N_2 + H_2$$

Whether primary mode (a) occurs or not could be decided definitely by the para hydrogen conversion technique. Were it not for the low absorption coefficient 1.05 for $\lambda = 2144^{\circ}$ A and 9 m.m. pressure of hydrazine and its comparatively efficient inhibition of the conversion at pressures of 10 m.m. the present experiments would have been conclusive. It may be remarked, however, that in an isolated experiment where a higher spark intensity was attained, a definite conversion was detected. The conditions of this experiment have not been successfully repeated.

The same alternative primary and secondary mechanisms are possible in the mercury sensitised photolysis. The observed quantum efficiency of 0.4 (page 73) proves this is not a chain reaction.

I wish to record my keen appreciation of the excellent facilities put at my disposal by the Chemistry Department and of the co-operation of its academic and non-academic staff. To Dr Ludlam I owe a debt of gratitude for his unfailing patience and understanding in times of difficulty. And to Dr Melville I am especially indebted for constant encouragement and inspiring direction throughout this work. Finally, I welcome this opportunity of offering my sincere thanks to the Trustees of the Carnegie Trust for the grant of a Research Scholarship.

References.

1. Warburg. Sitzungsber d. preuss. Akad. der Wissensch., Bf2, 745 (1911) and 216 (1912).

2. Bodenstein & Lind. Z. Physik. Chem., 57, 168 (1907).

3. Bonhoeffer & Farkas. ibid., 134 A, 337 (1927).

4. Rabinowitch & Wood. Trans. Farad. Soc., 30, 120 (1934).

5. Geib & Harteck. Z. Physik. Chem., Bodenstein Festband, 849 (1931).

6. Melville. Trans. Farad. Soc., 28, 885 (1932).

7. Farkas, L. and Harteck. Z. Physik. Chem., 25B, 257 (1934).

8. Welge & Beckmann. J. Am. Chem. Soc., 58, 2462 (1936).

9. Jungers & Taylor. J. Chem. Phys., 2, 373, 452 (1934).

10. Gedye & Rideal. J. Chem. Soc., 1160 (1932).

11. Koenig & Brings. Z. Physik. Chem., Bodenstein Festband, 595 (1931).

12. Mund & van Tiggelen. Bull. Soc. Chim. Belg., 46, 104 (1937) and 228 (1937). Annales. Soc. Scien. Bruxelles, 57, 92 (1937).

13. Wiig. J. Am. Chem. Soc., 57, 1559 (1935).

14. Ogg, Leighton & Bergstrom. ibid., 56, 318 (1934).

15. Mund, Brenard & Kaertkemeyer. Bull. Soc. Chim. Belg., 46, 211 (1937).

16. Leighton, P.A. Exposes de Photochemie, Hermann & Cie, Paris (1938).

17. Elgin & Taylor. J. Am. Chem. Soc., 33, 1316 (1932).

18. Wenner & Beckmann. J. Am. Chem. Soc., 54, 2787 (1932).

19. Dixon. ibid., 54, 4262 (1932).

20. Bolland & Melville. Trans. Farad. Soc., 33, 1316 (1937).

21. Forbes & Heidt. J. Am. Chem. Soc., 56, 2363 (1934).
and also
Heidt & Daniells. ibid., 54, 2384 (1932).
Leighton & Forbes. ibid., 52, 3139 (1930).
Buchi, P.F. Z. Physik. Chem., 111, 269 (1924).

22. Melville & Walls. Trans. Farad. Soc., 29, 1255 (1933).

23. Zemanski. Phys. Rev., 36, 919 (1930).

24. Farkas & Melville. Proc. Roy. Soc., A 157, 625 (1936).

25. Rudberg. Z. Physik., 24, 247 (1924).

26. Leighton, Smith & Leighton. J. Am. Chem. Soc., 60, 2566 (1938).

27. Bolland & Melville. Proc. Roy. Soc., A 160, 384 (1937).

28. Melville. ibid., A 139, 541 (1933).

29. Farkas, A. Light and Heavy Hydrogen. Cambridge Univ. Press (1935).

30. Penney & Sutherland. J. Chem. Phys.,

32. Ogg, Leighton & Bergstrom. J. Am. Chem. Soc., 55, 1754 (1933).

33. Wiig & Kistiakowsky. ibid., 54, 1806 (1932).

34. Wiig. ibid., 59, 827 (1937).

35. Dickinson & Mitchell. Proc. Nat. Acad. Sci., 12, 692 (1926).

36. Bates & Taylor. J. Am. Chem. Soc., 49, 2438 (1927).

37. Taylor. J. Phys. Chem., 42, 788 (1938).

38. Jeans. Dynamical Theory of Gases. 4 ed., Chap.XIII.

39. Mackenzie & Melville. Proc. Roy. Soc. Edin., 52, 343 (1932).

40. Mack. J. Am. Chem. Soc., 47, 2473 (1925).
Edwards & Worswick. Proc. Phys. Soc., 38, 16 (1925).
Rankine & Smith. Phil. Mag., 42, 601 (1921).

41. Melville & Birse. Nature, 142, 1080 (1938).
Reprint below.

42. Melville. Science Progress, 123, 499, (1937).

43. Melville. Proc. Roy. Soc., 138A, 374, (1932).

44. Melville. ibid., 152A, 325, (1935).

45. Farkas and Melville. Experimental Methods in Gas Reactions p. 79. Macmillan (1939).

46. Steacie. J. Chem. Phys., 6, 37, (1938).

Review Papers.

A. Luyckx. Questions. Scien., Nov. 1935, and May, 1936.

P.A. Leighton. Exposes de Photochimie, Hermann & Cie, Paris (1938).

H.S. Taylor. J. of Phys. Chem., 42, 788, (1938).

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Photochemistry of Ammonia

THE mechanism of the photochemical decomposition of ammonia has been the subject of considerable discussion lately[1], from which it would appear that the nature of the reaction is almost completely elucidated. The experiments to be mentioned below were designed to settle the few remaining uncertain points regarding the reaction. In point of fact, however, they have opened the results to a new interpretation.

The relevant experimental evidence, discussed in the references cited above, may be summarized thus. From the diffuse nature of the absorption spectrum and the absence of fluorescence, it was concluded that each molecule on absorbing a quantum dissociated into NH_2 and H. The low quantum yield—for example, 0·3 at 20° C. and 100 mm. pressure—was interpreted as due to a back reaction, which was supported by the fact that atomic hydrogen inhibited the reaction. Using para hydrogen to measure the stationary concentration of atomic hydrogen, it was found that this concentration was much smaller than that calculated on the assumption that H atoms disappear by the reactions $H + H + X \rightarrow H_2 + X$ and $H + NH_2 + X \rightarrow NH_3 + X$, where X is a third body. This anomaly was explained by assuming that NH_2 radicals combine to form hydrazine, which in turn rapidly reacts with atomic hydrogen, thereby maintaining a low stationary atom concentration.

In order to compute the magnitude of this latter process, the effect has been measured of hydrazine on the stationary atomic hydrogen concentration (estimated by para hydrogen conversion) produced by photo-excited mercury atoms. The results showed that the low concentration is not due to hydrazine, for the pressure of hydrazine required to account for the low concentration of hydrogen atoms could not possibly be formed during the course of a normal ammonia experiment.

This point was made doubly sure in the following way. If hydrazine is responsible for the low concentration, then ammonia *undergoing photo-dissociation* should also inhibit the para hydrogen conversion photo-sensitized by mercury atoms. A mixture of ammonia and para hydrogen was therefore exposed first to a mercury resonance lamp and then simultaneously to the lamp and to a zinc spark which dissociated the ammonia. There was no appreciable inhibition of para conversion when the ammonia was being dissociated, even though conditions were such

that inhibition of ammonia decomposition by atomic hydrogen could be detected.

The conclusions to be drawn from these experiments are that the low hydrogen atom concentration is not due to the presence of hydrazine, which substance plays no significant part in the photo-chemistry of ammonia, except under special conditions, and that the secondary reactions only involve $H + H \rightarrow H_2$, $NH_2 + NH_2 \rightarrow 2H_2 + N_2$ and $H + NH_2 \rightarrow NH_3$.

Another series of experiments gave the probable clue to the dilemma. Using the same intensity of radiation for exciting mercury atoms and for dissociating ammonia, it was observed that the ratio of the rates of para hydrogen conversion is very nearly equal to that expected if only one quarter of the ammonia molecules absorbing light yield the products NH_2 and H.

These experiments therefore suggest that only a fraction (given approximately by the quantum yield) of the ammonia molecules undergo primary dissociation to H and NH_2, which react in the fashion mentioned above. The remainder lose their energy by chemically ineffective processes.

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[1] Taylor, H. S., *J. Phys. Chem.*, **42**, 783 (1938). Leighton, P. A., "The Determination of the Mechanism of Photochemical Reactions", 27 (Paris: Hermann et Cie).

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